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Part 1. Haze Properties

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HAZE OVER EASTERN NORTH AMERICA
Part 1. Haze Properties

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The fundamental properties of atmospheric aerosols pertinent to atmospheric optics are the size, shape, and refractive index for the entire aerosol population at a given point. Once these properties are established, their interaction with visible radiation can be calculated, and the relevant optical properties can be measured. The most important properties are the concentration and size distribution of particles within the accumulation mode of 0.1 to 1.0mm in diameter. The chemical composition of the aerosol population has a weak influence on optical properties through changing the refractive index, but it is vital for the identification of the origin of the lightscattering aerosol. This report reviews the properties of aerosols relevant to their optical behavior. Regulations in these properties suggest that relatively simple parameterizations can be developed which will relate optical properties to aerosol mass. These relationships can then be used with aerosol models to predict visibility and with optical measurements to infer aerosol mass.

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ABSTRACT

The fundamental properties of atmospheric aerosols pertinent to atmospheric optics are the size, shape, and refractive index for the entire aerosol population at a given point. Once these properties are established, their interaction with visible radiation can be calculated, and the relevant optical properties can be measured. The most important properties are the concentration and size distribution of particles within the accumulation mode of 0.1 to 1.0 μm in diameter. The chemical composition of the aerosol population has a weak influence on optical properties through changing the refractive index, but it is vital for the identification of the origin of the light-scattering aerosol. This report reviews the properties of aerosols relevant to their optical behavior. Regularities in these properties suggest that relatively simple parameterizations can be developed which will relate optical properties to aerosol mass. These relationships can then be used with aerosol models to predict visibility and with optical measurements to infer aerosol mass.

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1. INTRODUCTION

This report is a review of the optical characteristics of atmospheric aerosols, the physical and chemical properties and behavior which influence optical properties, and the relations between optical properties and chemical and physical properties. We search for regularities in aerosol properties that will assist us in parameterizing the optical behavior of the atmospheric aerosol. Such parameterizations are needed to transform aerosol mass calculated in regional or urban models into visual range and other visibility-related air quality parameters. Parameterizations are also needed to estimate aerosol mass loading from optical measurements such as obtained from teleradiometers or from images taken by satellites.

2. CONCLUSIONS

The atmospheric aerosol exhibits regularities in its physical, chemical and optical properties. These regularities should permit relatively straight- forward parameterization of optical properties based on the total aerosol mass and the relative humidity. Because of the importance of sulfate for scattering and carbon for absorption, knowledge of the concentration of these two species, along with relative humidity, should provide a useful first estimate of optical extinction from which visual range may be inferred.

The idea of the self-preserving size distribution must be replaced by that of the accumulation mode in which atmospheric particulate matter piles up on accumulation. The accumulation mode of well-aged particulate matter does have a relatively constant mass mean diameter. However, as the total mass concentration increases there appears to be small increase in the mass mean diameter and a corresponding shift in the phase function toward more scattering in the forward direction. Information on phase function variations are important for calculating aerosol mass from optical properties, for determining changes in visual air quality such as contrast in objects at distances less than the visual range andfor estimating changes in haze color and intensity as a function of viewing angle. The regularities in these relationships appear to be adequate to permit parameterization of phase function in terms of aerosol mass loading.

3. RECOMMENDATIONS

It is recommended that the visibility research program proceed to develop parameterizations which relate optical extinction to aerosol mass and phase function to aerosol mass, use these parameterizations to calculate visibility from predictive aerosol models and to estimate aerosol mass loading from satellite imagery.

4. AEROSOL PROPERTIES

The fundamental properties of atmospheric aerosols pertinent to atmospheric optics are the size, shape, and refractive index for the entire aerosol population at a given point. Once these properties are established, their interaction with visible radiation can be calculated, and the relevant optical properties can be measured. The chemical composition of the aerosol population has only a weak influence on optical properties through changing the refractive index, but it is vital for the identification of the origin of the light-scattering aerosol.

Size distribution and particle shape

The size of atmospheric aerosols ranges over five orders of magnitude. The smallest observed particles are on the order of $10A^0$ in diameter, and they could well be called molecular clusters.

At the other extreme, large dust particles of 100 μm or more may be kept suspended in the air for extended periods of time. Within the five decades of size range, there are 'windows' in which the particles are comparable to the wavelength of visible radiation (0.4- 0.7 μm), to the mean free path of atmospheric gases (0.06 μm), and the wavelength of the outgoing infrared radiation from the earth (6 - 40 μm).

Recent intensive studies on the physical-chemical properties and behavior of man-made aerosols have revealed some important regulatities. In studying the characteristics of the Los Angeles smog aerosol, Whitby et al., 1972 discovered and substantiated by a variety of data that most of the atmospheric aerosol volume and mass is distributed bimodally; the lower mass mode being in the size range 0.1 - 1 μm while the upper mode was over 5 μm as shown in Figure 1. The saddle point between the two volume or mass modes is generally between 0.8 - 3 μm. The significance of their finding of bimodal aerosol mass distribution is that the two modes were subsequently identified as having distinctly different physical characteristics (particle shape, volatility) and chemical composition; ordinarily the two modes are produced by different sources, and finally the lower (fine) and upper (coarse) mass modes are associated with distinctly different effects. In Figure 1, the area under each curve represents the fraction of the property (e.g.) number, surface, and volume) that is contained within a given size range. It is thus seen that the total number is contributed primarily from the 0.1 μm size range. In some rare instances the surface distribution can also be trimodal.

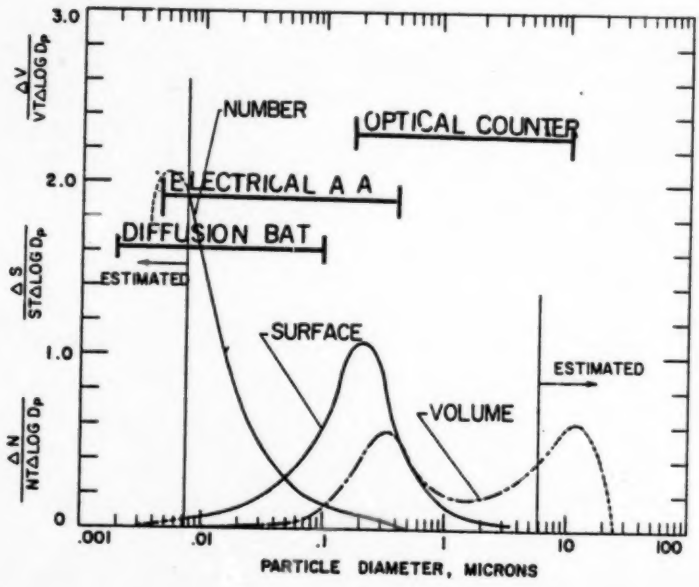

Figure 1. Number, surface and volume distributions for typical aerosols in the lower atmosphere. The area under each curve segment is proportional to the fraction of the property (number, N; surface, S; volume, V) that is contained within a given size range. (Whitby et al., 1972).

Beyond these generalities it is important to note that the relative magnitude of the two

modes (the area under each mode) may vary drastically from one location to another and the mean size of the two mass modes may also vary somewhat.

At present, there is no generally accepted expression (formula) which would universally describe the complete size distribution of atmospheric aerosols. However, visual inspection of the size distributions shown in Figure 2 suggests that the volume and surface distributions could be reasonably well approximated by a set of lognormal distrbutions displaced in particle size. This concept has been used to fit an extensive set of measured ambient aerosol size distributions (Table 1). The size range for the three lognormal fitting parameters were called the nuclei mode, the accumulation mode, and the coarse particle mode as illustrated in Figure 2. For aerosol optics the nuclei mode is generally inconsequential because it contains very little aerosol mass and the light scattering efficiency of those particles is vanishingly small. If, however, the nuclei contains absorbing particles such as soot, their contribution to extinction would be almost the same as if they were in the accumulation mode.

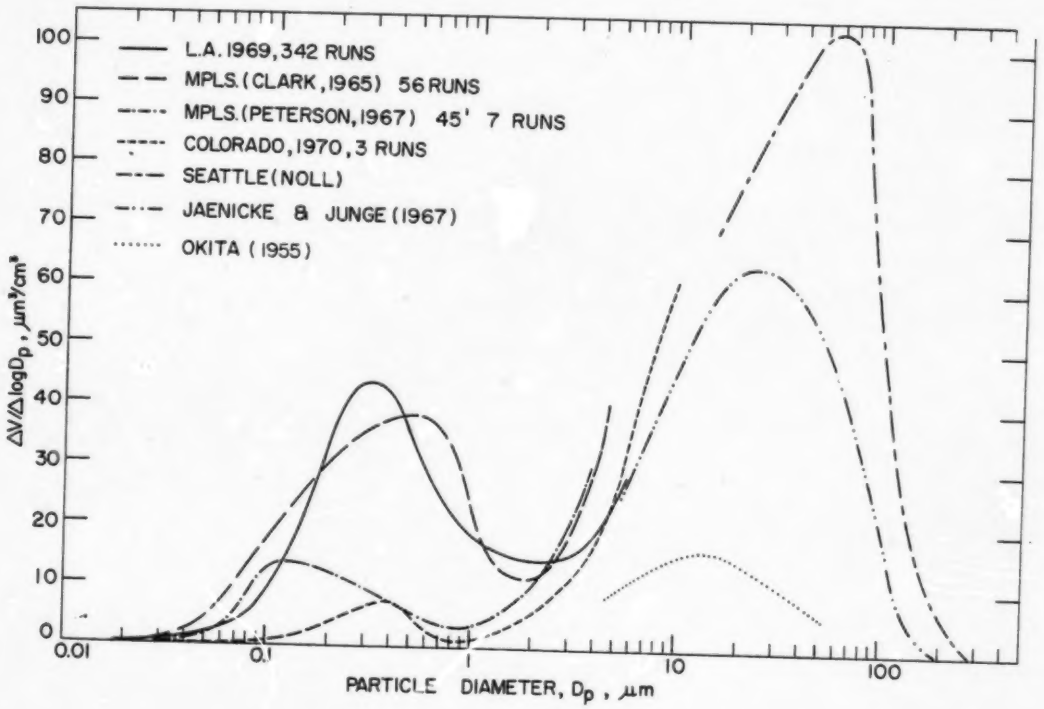

Figure 2. Comparison of aerosol volume distributions measured by several investigators in different locations shows the bimodal aerosol spectrum for a variety of locations.

Atmospheric optics is influenced most severely by the presence of accumulation mode aerosols in the 0.1 - 1 μm size range. Particles in that size range are not only the most efficient scatterers per unit mass, but fine particles also tend to accumulate in that size range, which prompted Whitby (1973) to call that the accumulation mode. The volume concentration in the accumulation mode ranges from 0.1 $\mu m^3/cm^3$ for marine background aerosols (which corresponds to concentrations of 0.1 $\mu g/m^3$ at unit density) to about 100 $\mu m^3/cm^3$ in regional

Table 1 Lognormal fitting parameters (Whitby and Sverdup, 1978)

Type of Aerosol	Nuclei Mode			Accumulation Mode			Coarse Particle Mode		
	DG+ (μm)	σ_g	V ($\mu m^3/cm^3$)	DG+ (μm)	σ_g	V ($\mu m^3/cm^3$)	DG+ (μm)	σ_g	V ($\mu m^3/cm^3$)
Marine, surface background	0.019	1.6*	0.0005	0.3	2.0*	0.10	12.0	2.7	12.0
Clean continental background	0.03	1.6	0.006	0.35	2.1	1.5	6.0	2.2	5.0
Average background	0.034	1.7	0.037	0.32	2.0	4.45	6.04	2.16	25.9
Background and aged urban plume	0.028	1.6	0.029	0.36	1.84	44.0	4.51	2.12	27.4
Background and local sources	0.021	1.7	0.62	0.25	2.11	3.02	5.6	2.09	39.1
Urban average	0.038	1.8	0.63	0.32	2.16	38.4	5.7	2.21	30.8
Urban and freeway	0.032	1.74	9.2	0.25	1.98	37.5	6.0	2.13	42.7
Labadie plume (1976)†	0.015	1.5	0.1	0.18	1.96	12.0	5.5	2.5	24.0

* Assumed.

† Typical distribution observed in the plume from the Labadie coal-fired power plant near St. Louis, Missouri.

+DG is the geometric mean diameter

hazes. In spite of an almost three orders of magnitude of volume concentration variability the mean size and the fitted logarithmic standard deviation of the accumulation mode aerosol was found to be remarkably constant: the volume mean size ranged from 0.18 - 0.3 μm while σ_g was between 1.84 and 2.11.

The relative invariance of the particle mean size and size distribution of accumulation mode aerosols is further illustrated in Figure 3. Measurements of the aging aerosols size distribution in the St. Louis urban plume by Auer (1977) show that there is a variablity of the aerosol volume concentration (area under the curve) with increasing distance from the city, but mean size and the shape of the size distribution remain essentially constant. Presumably this increase in volume concentration is a direct consequence of the condensation of photochemically generated material on an aerosol of broad initial size distribution (Husar et al., 1972).

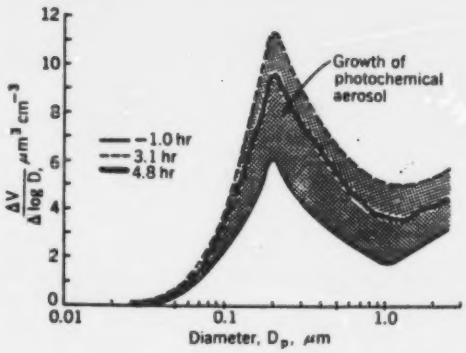

Figure 3. The volume of the aerosol in the St. Louis urban plume is greater at 3.1 and 4.8 hours than at 1 hour after emission. However, the mean size and the shape of the size distribution is unchanged. (Auer, 1977)

The aerosol size distribution in the fine and coarse particle modes can vary independently because they generally originate from different sources. In the ACHEX study in Los Angeles (Hidy et al., 1975), for instance, it was found that the size distribution can change from typical desert aerosol to the usual bimodal urban-regional aerosol spectrum within half an hour (Figure 4). The key feature of the dusty desert aerosol is that there is an appreciable mass or volume in the coarse particle mode but essentially none in the fine particle mode.

The desert aerosols in a relatively calm atmosphere are characterized by extremely low concentrations in both the fine particle and coarse particle mode. In the Four Corners region, for instance, as part of project VISTTA, Macias et al., (1979) have reported aerosol volume concentrations of 2.6 and 2.5 $\mu m^3/cm^3$ in the fine and coarse modes, respectively. This corresponds to about 5 μm^3 in each mode at aerosol density of 2 g/cm^3. It is of considerable interest to note that even in the calm and pristine atmosphere of the southwestern desert, the aerosol size distribution can be bimodal with comparable amount of matter in the two modes (Figure 5).

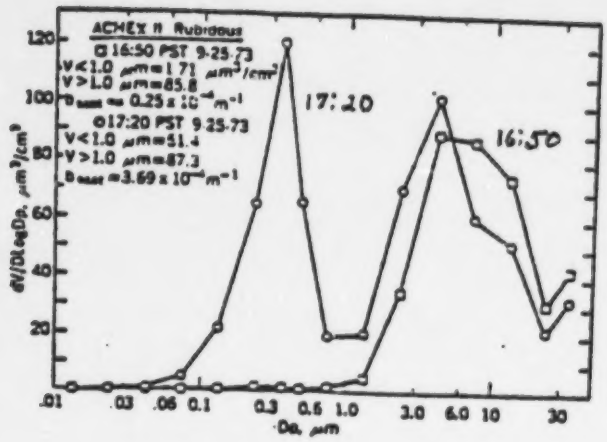

Figure 4. In the California ACHEX study the measured aerosol distributions have shown that the fine and coarse particle modes are essentially independent. In Rubidoux, for example, the size distribution has been observed to change from a fine particle-free distribution at 16:50 (Sept. 25, 1973) to the usual bimodal distribution at 17:20, (Hidy et al., 1975)

Atmospheric aerosols exhibit a variety of shapes. Most common fine particles are spherical liquid droplets consisting of salt or acid solutions. The photochemically produced aerosol such as the Los Angeles smog also consists of droplets. Several of the aerosol salts (ammonium sulfate and sodium chloride) exhibit deliquessence (Junge, 1963; Covert, 1974). This behavior is manifested by a rapid transition from crystalline form to droplet form at RH of 60-80% . Dry sodium chloride crystals are almost exactly cubical; ammonium sulfate crystals are approximately cubical but have more rounded edges. Combustion leads to the formation of very small spherical carbon particles which aggregate to form chains or clumps. When suspended in air, chain aggregates may bend, twist, and rotate due to asymmetric molecular bombardment and fluid shear.

A sample of atmospheric fine particles impacted onto a grid and viewed through an electron microscope is shown in Figure 6a. The chain aggregate in the center probably originated from automobile exhaust. Unfortunately atmospheric liquid particles lose their identity when viewed in an electron microscope. However, such liquid particles leave a flat, circular residue as evidence of their original form.

Size segregated samples of coarse atmospheric particles are shown in the scanning electron microscope, Figure 6b. They are mainly composed of irregularly shaped crystalline or fibrous materials.

From the point of view of aerosol optics the key question is whether an aerosol particle is spherical. For such particles rigorous Mie theory is applicable and the optical properties can be readily calculated from their size and reflective index. Measurements in St Louis by Allen (1977) show that in the accumulation mode less than 5% of aerosol population exhibits nonspherical

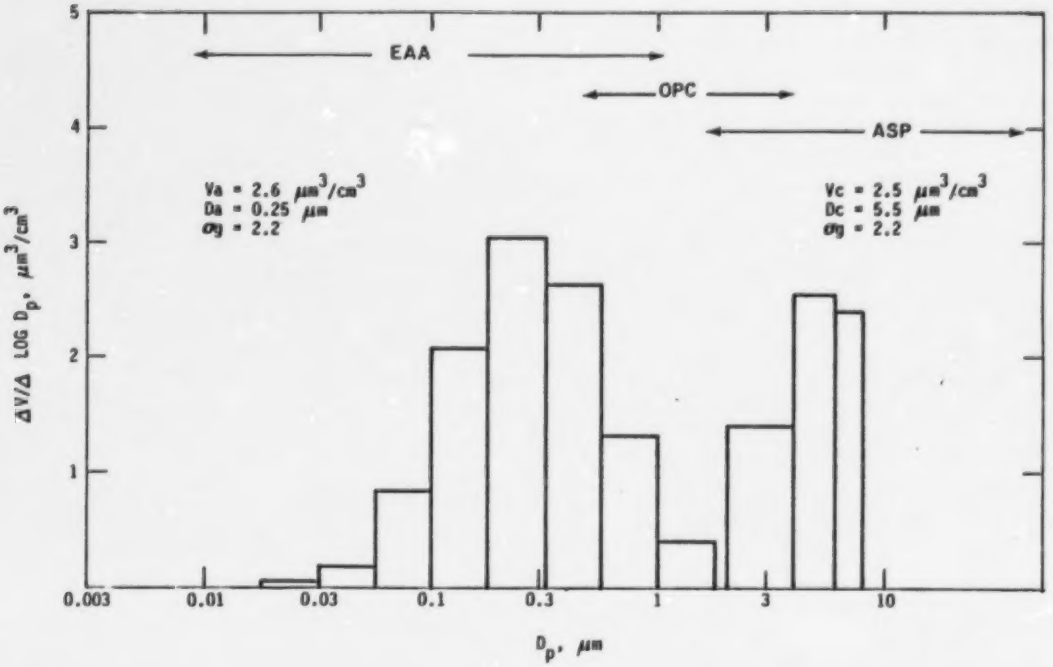

Figure 5. The average size distribution of aerosol measured during the flight in the Four Corners region shows a bimodal distribution with low concentration in both modes (Macias et al., 1979).

shape. Coarse particles are almost exclusively nonspherical and therefore the application of the Mie theory to calculate their optical properties is only a crude approximation. Currently there is an extensive body of experimental data on the optical properties of the nonspherical particles (e.g. Pinnick et al., 1976).

In summary, the atmospheric aerosol mass or volume distribution over the continental U.S. is generally bimodal, the fine particle volume mean diameter being almost invariant in size at about 0.3 μm. Most accumulation mode particles are spherical droplets.

Chemical Composition of Light Scattering Aerosols

The knowledge of the chemical composition of light scattering aerosols is essential to the understanding of the cause of visibility impairment. It is not so much that the chemical composition of the aerosol changes the optical properties; rather the chemical composition serves as a tracer of the probable origin of the light scattering aerosol. In fact, for atmospheric haze in general, the chemical composition is the most important clue we have currently available regarding its probable origin.

The method by which the ambient aerosol chemical composition is used as a tracer for its origin was formulated by Friedlander (Heisler et al., 1973). Characteristic tracer elements such as vanadium (which comes primarily from fuel oil) and lead (which comes primarily from auto

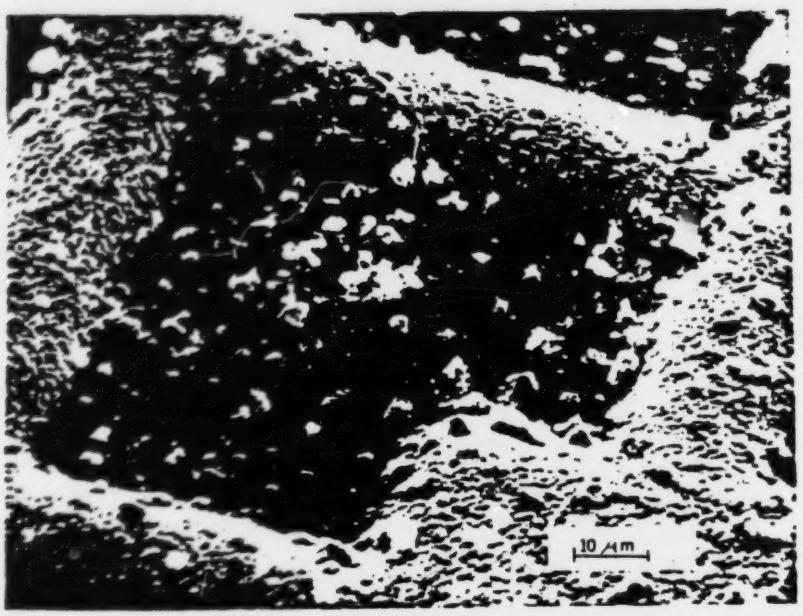

Figure 6a. Transmission electron micrograph of size classified submicron aerosols. Most of the submicron aerosol volume is made up from liquid droplets which leave circular residues and of chain agglomerates. The white area in the center is where the collodion film is broken and the chain agglomerate aerosol is directly exposed to electron beam. (Husar, 1974).

exhaust) can be used to tell how much these sources contribute to the ambient aerosol.

The first comprehensive study of the size-chemical composition of the haze aerosol was conducted in the Los Angeles air basin as part of project ACHEX (Hidy et al., 1975). In their study of the nature and origins of visibility-reducing aerosols in Los Angeles, White and Roberts(1981), have constructed a chemical mass balance for the measured aerosol at seven locations in the basin (Figure 7). The key contributing species for the total aerosol mass concentration were nitrates, sulfates, organics and other unidentified substances. Based on statistical analysis of the integrated scattering b_{scat} and chemical composition data, they have concluded that sulfates are the most efficient scatterers among the measured chemical species.

A separate chemical-mass balance for fine and coarse particles collected in Charleston, W. Virginia, reported by Lewis and Macias (1979), is shown in Figure 8. Of the fine particle mass concentration (33 $\mu g/m^3$) about 30% was sulfate; about 13% was ammonium; 18% was carbonaceous material, while the rest consisted of trace constituents and undetermined chemical species. The coarse particle mass of 27 $\mu g/m^3$ was found to be largely associated with elements that occur in the Earth's crust. They have concluded that the various elements were found predominately in one size fraction or the other. Carbon was the only major element that was about equally distributed between the two size fractions.

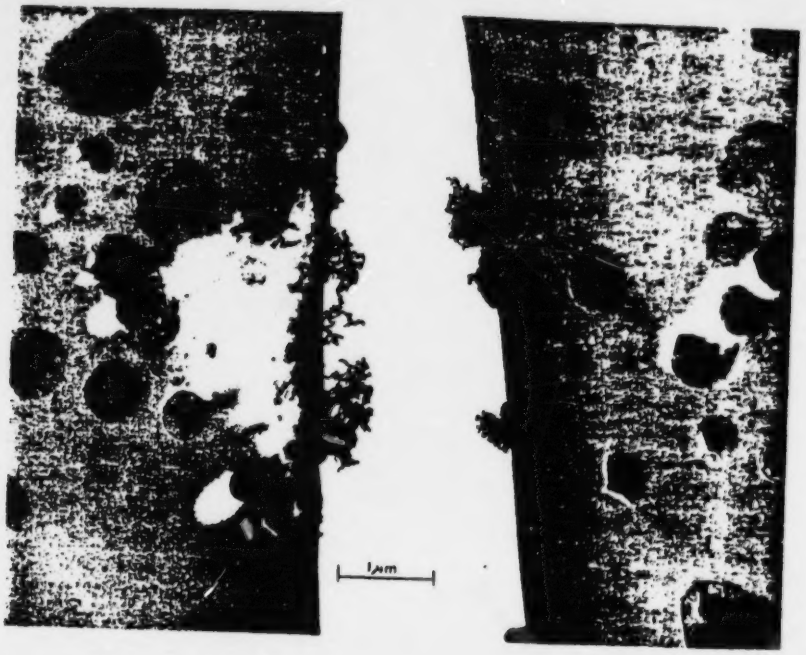

Figure 6b. Scanning electron micrograph of size classified (greater than 2 μm) atmospheric aerosol collected by an impactor shows that most coarse particles are irregularly shaped crystals. (Husar, 1974).

A more detailed size-chemical composition distribution was reported by Patterson and Wagman (1977) for the New York metropolitan area aerosol (Figure 9). Elemental lead was found primarily in the size range below 0.5 μm. Sulfate and ammonium ions exhibited similar size distribution ranging between 0.2 and 0.7 μm. From the previous discussion we should note that the size range at which sulfate and ammonium occurs is also the window of peak light scattering efficiency per unit mass. Zinc was found to be distributed around 1.0 μm while nitrate was contained in both fine and coarse particle modes. Iron, manganese and the other crustal elements were exclusively in the coarse particle fraction and they had all similar size distributions.

For several years an extensive air pollution monitoring program was conducted in St. Louis as part of project RAPS (Regional Air Pollution Study.) Size segregated aerosol samples (Stevens et al., 1978) were automatically collected by the dichotomous samplers and analyzed for the elemental composition and mass concentration of fine and coarse particles.

The results from the ten station monitoring network, Figure 10, analyzed by Dzubay (1980), show the distribution of the aerosol species within the St. Louis metropolitan area. Here again we note that sulfur compounds are the dominant species of the fine aerosol fraction, contributing about 60% of the mass. For stations 103-112, within the central city, motor vehicle contribution was estimated to be about 10% of the fine particle mass. For the peripheral stations, 25 kilometers removed from the city center, (station 122 and 124) the sulfate concentrations were comparable to those within the city, but motor vehicles accounted for only a few percent of the

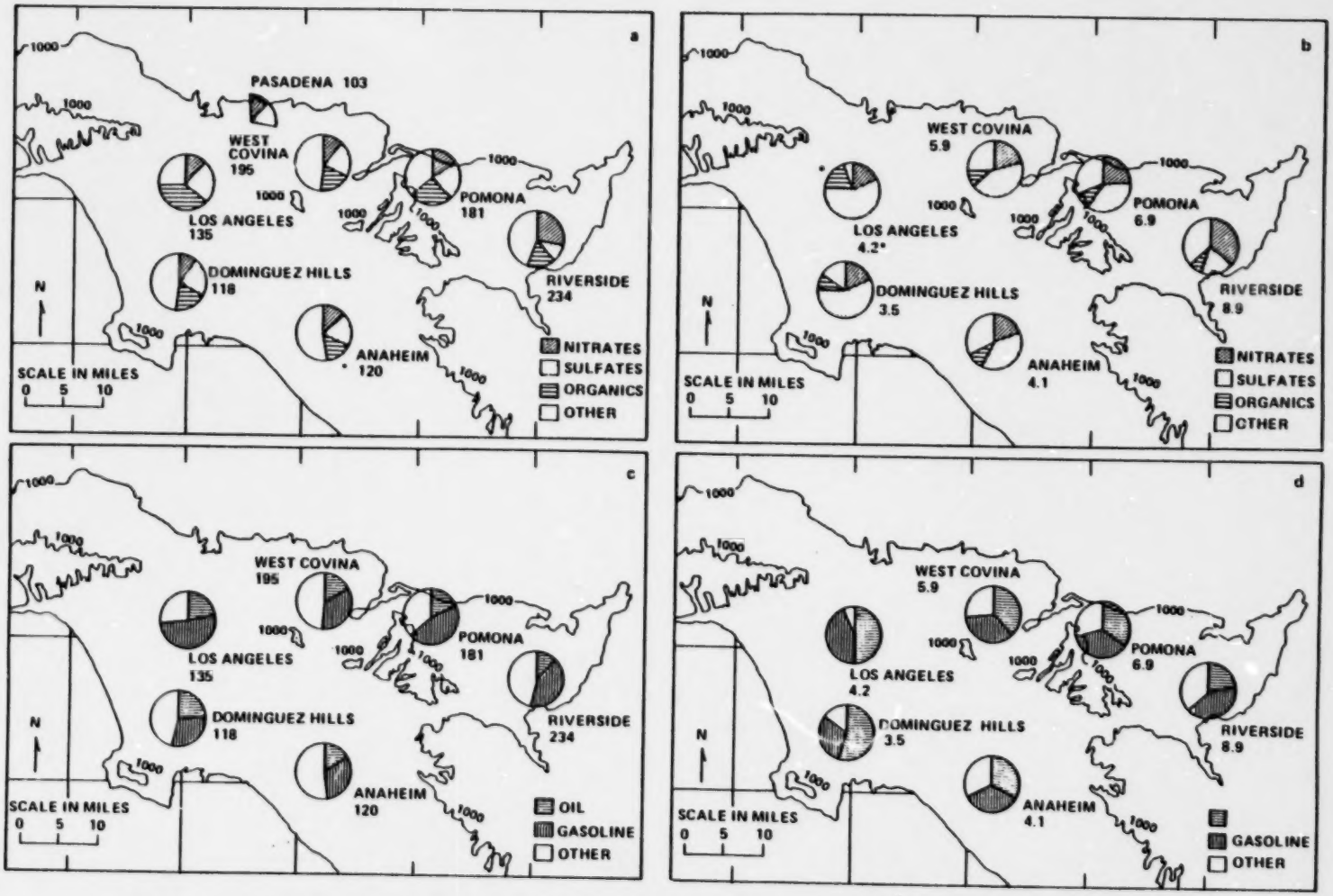

Figure 7. Geographical distribution of mass concentration (a) and light scattering coefficient (b) in the Los Angeles basin. The pie diagrams show the relative contributions of nitrates, sulfates, organics and other compounds. Sulfates evidently contribute only about 25% of the total mass but cause about half of the light scattering. The contributions of source types (oil, gasoline and other) to the mass concentration (c) and light scattering coefficient (d) are also shown. (White and Roberts, 1981).

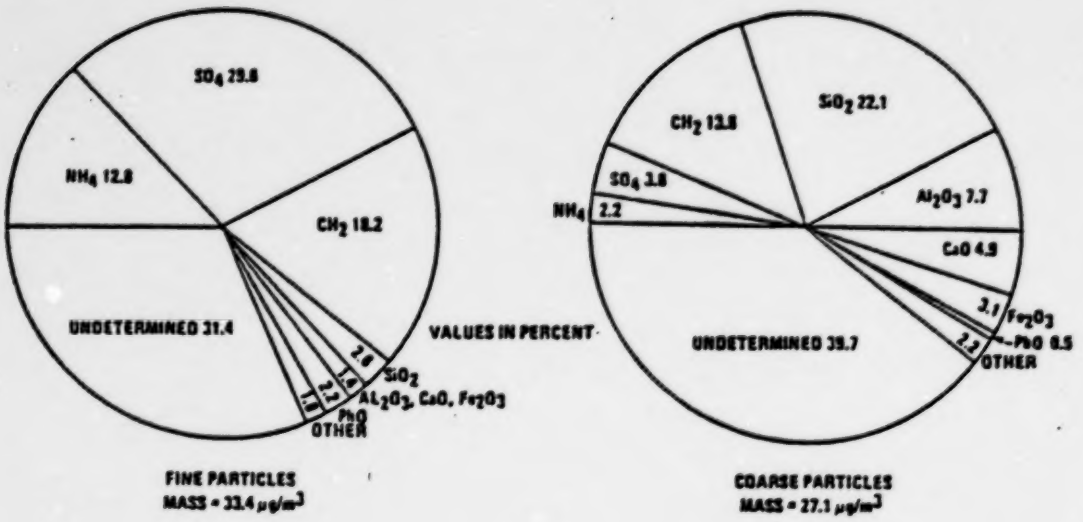

Figure 8. Chemical mass balance for fine and coarse particles collected in Charleston, WV (Lewis and Macias, 1979).

fine particle mass. It is thus concluded, that the automobile contributions were of local origin while the sulfate is distributed regionally, and the addition of the sulfate by the St. Louis metropolitan area is only 10-20% over the "regional background". In his mass balance analysis, Dzubay (1980) was able to account for practically all the coarse particle mass by contributions of crustal shale and limestone. Figure 10 a and b also contain mass and chemical contribution composition data for a Smoky Mountain National Park site at Elkmont, Tennessee. The fine particle mass concentration there was about 25 $\mu g/m^3$, comparable to the values in the St. Louis region outside the city. There again about 60% of the fine particle mass was contributed by sulfur compounds. The unshaded, unknown compounds may include carbonaceous compounds, nitrates and water. The coarse particle mass concentration at the Smoky Mountain site was only 6 $\mu g/m^3$, substantially below that in the St. Louis region.

From the above it is apparent that sulfur compounds constitute the most significant chemical component of the fine particle mass over the Eastern United States. Further, statistical evidence for the importance of sulfates for the fine particle mass arises from the analysis of RAPS data by Loo et al. (1978). (Figure 11) The particulate elemental sulfur was consistently about 10-12% of the fine particle mass for a sampling period of two months (equivalent to 40-50% of the fine particle mass being $(NH_4)_2SO_4$). Similar observations were made by Lewis and Macias (1980) for Charleston, W.V., and by numerous other investigators.

Much of the current concern pertains to the origin of the haze in pristine areas of the Western and Southwestern U.S. where many of the Class I areas are located. Reporting the results of project VISTTA, Macias et al. (1980) have presented size-chemical composition data for size segregated aerosol collected in the Four Corners area during aircraft flights (Figure

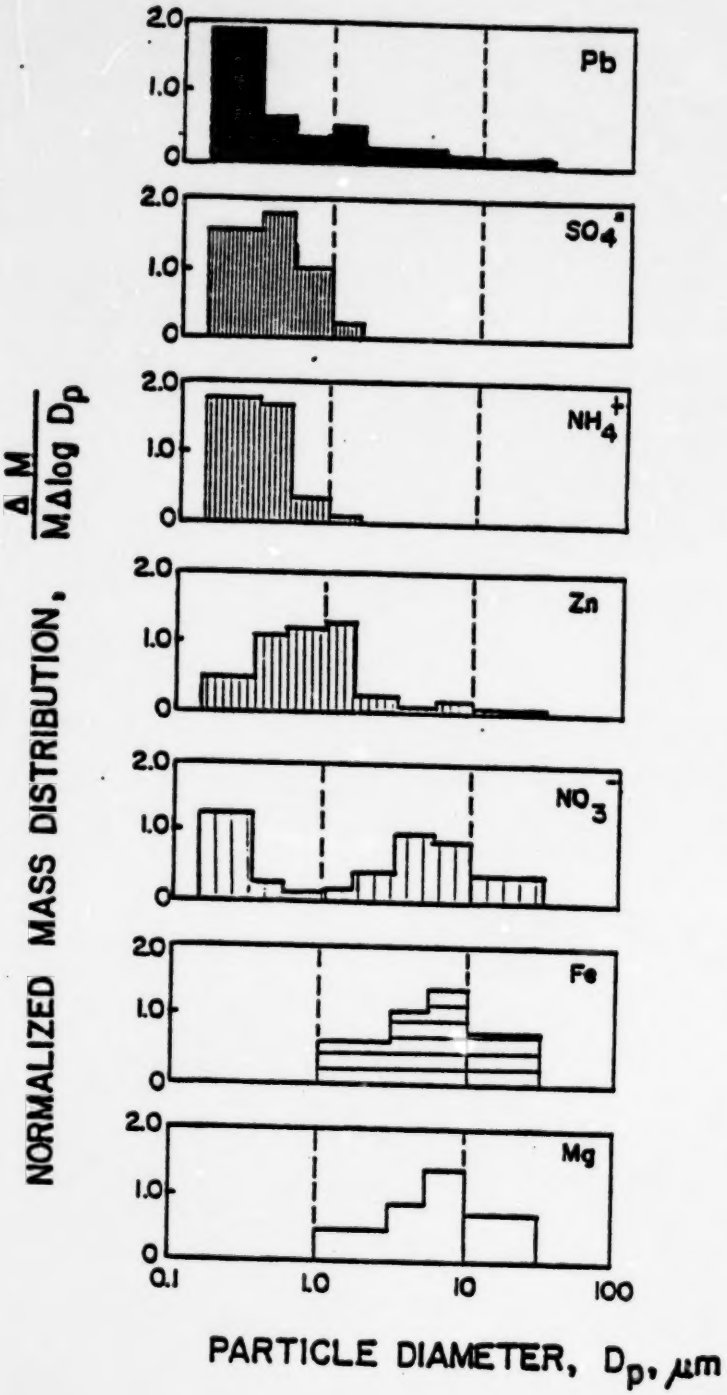

Figure 9. Normalized mass distribution functions of some species found in New York City aerosol. Sulfate and ammonium were found in the most efficient light scattering size range (0.4-0.7 μm). Adapted from Patterson and Wagman, 1977.

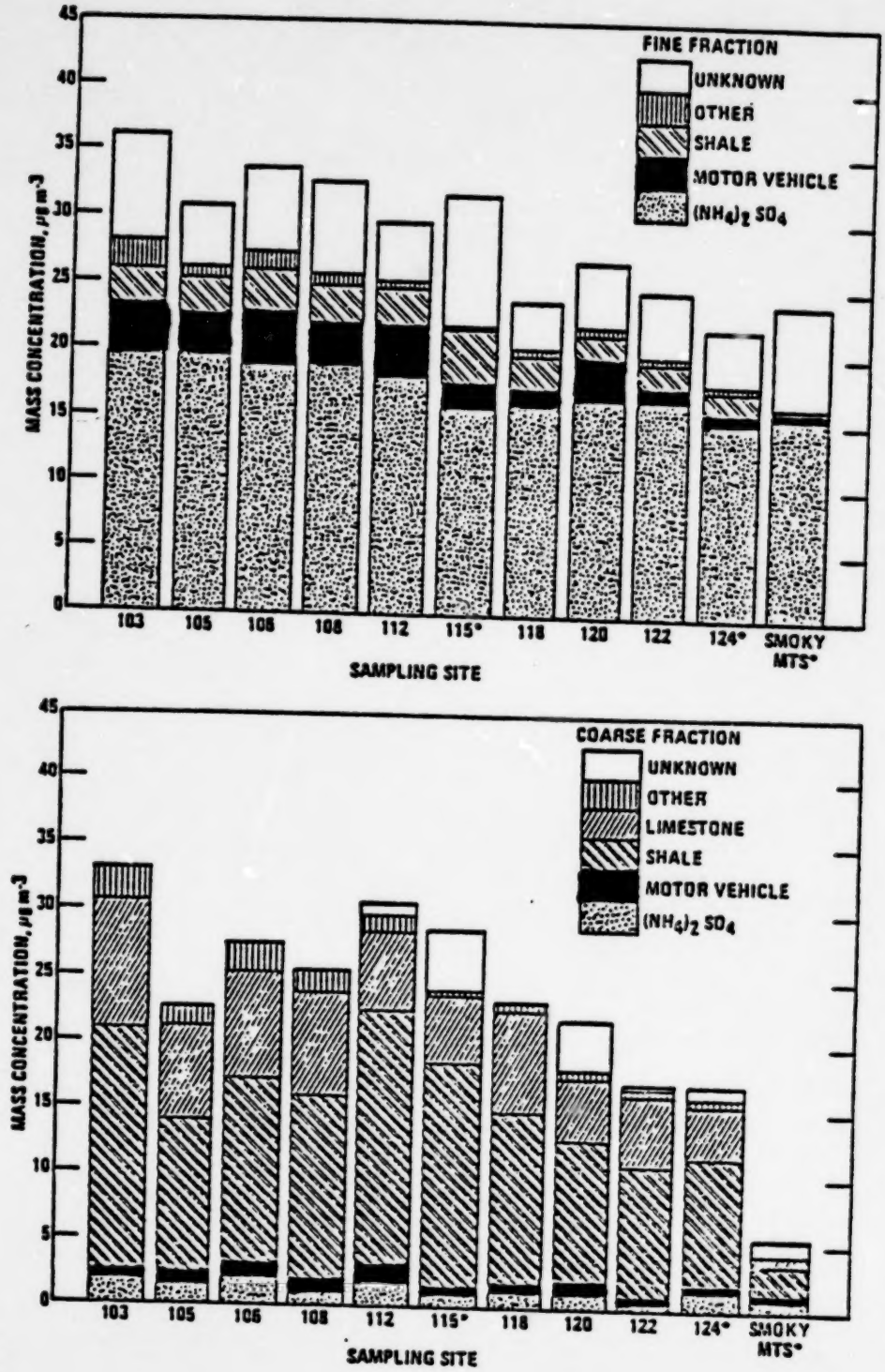

Figure 10. Source resolution of the St. Louis aerosol shows that less than 10% of the fine particle mass is due to primary automobile emissions; about 60% is from sulfur oxide sources. Almost all of the coarse particle mass is accounted for by dust from the earth's crust. (Dzubay, 1980)

12). As anticipated, the coarse particle fraction could be accounted for by the crustal element contributions. In the fine particle mass balance, about 40% of the 5.3 $\mu g/m^3$ was made of sulfate, another 10% of trace constituents, and 22% could not be accounted for. However, they have also reported a 29% contribution of silicon dioxide to the fine particle mass. This is unusual because the crustal elements normally accompanying silicon were not present in the fine particle samples. Macias et al. argued, therefore, that the fine particle silicon may possibly be due to direct emissions from combustion sources.

More detailed size distribution data for sulfur, silicon, and other compounds were reported by Winchester et al. (1979) for sites in New Mexico, Colorado, St. Louis and New Hampshire. Invariably, the particulate sulfur concentration was highest at the impactor stages between 0.25 and 1.0 μm (Figure 13). The size distribution of silicon, on the other hand, was consistantly the highest in impactor stages above 2 μm and lowest on the stages below 1 μm. Hence in the Winchester et al. (1979) data set the fine particle silicon content was practically negligible, even at the New Mexico and the Colorado sampling sites. The resolution of the difference between the data reported by Macias et al. (1979) and Winchester et al. (1979) will have to wait for further data from the western states.

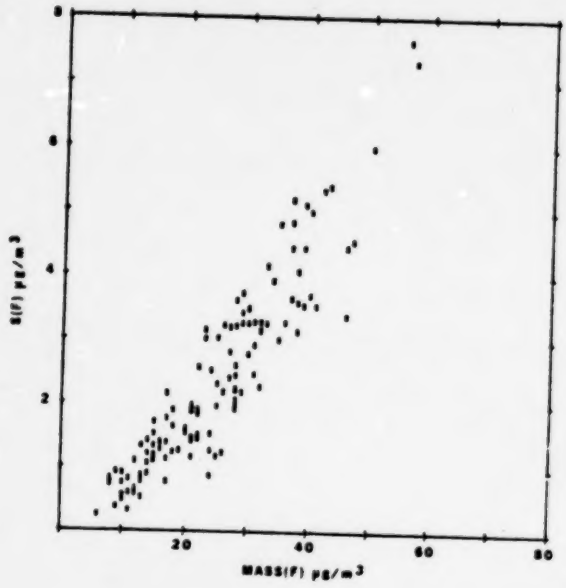

Figure 11. In the St. Louis area, monitoring data for about a two month period shows that elemental sulfur was 10-12% of the fine particle mass. (Loo et al., 1978)

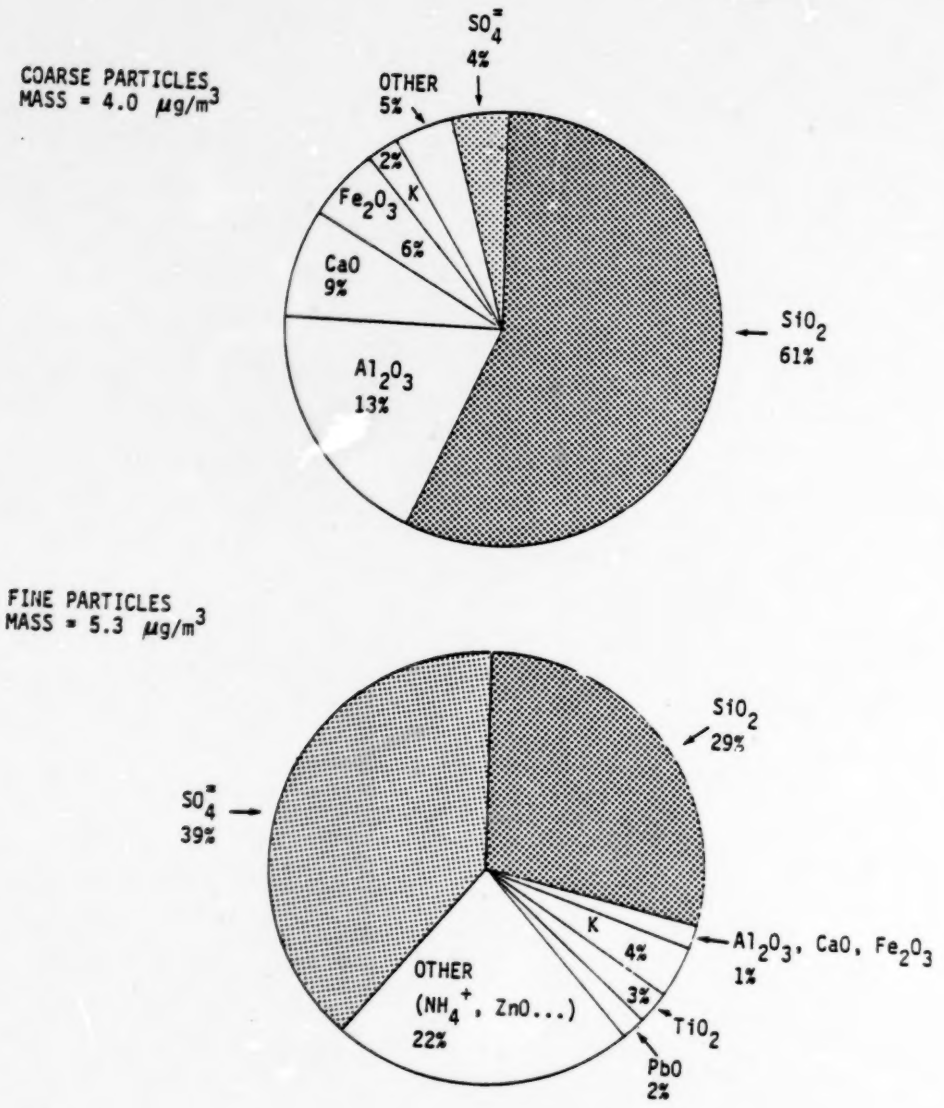

Figure 12. Chemical-mass balance for fine and coarse particles collected during flights in the Four Corners region. The total aerosol mass was estimated from in situ size distribution measurements. In this data set SiO_2 accounted for an estimated 29% of the fine particle mass. (Macias et al., 1979)

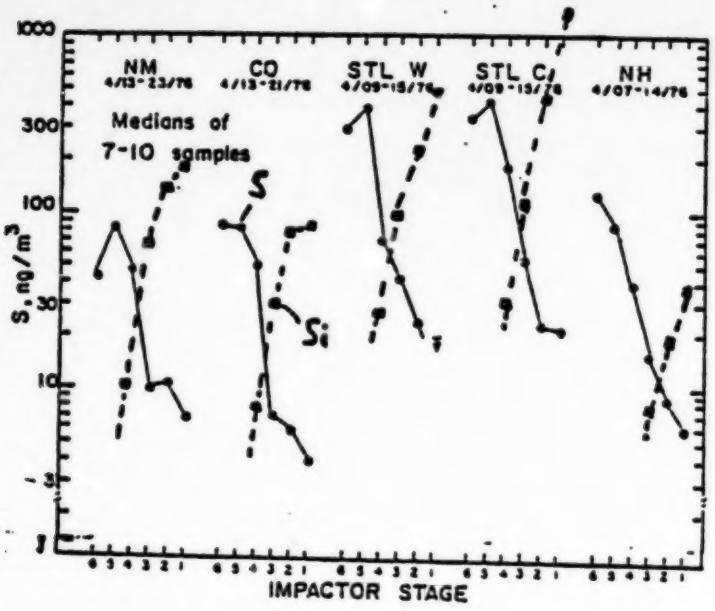

Figure 13. Detailed size distribution data for NM, CO, St. Louis and NH sites show that elemental sulfur is invariably contributed by submicron size aerosols. Silicon, on the other hand, is exclusively from coarse particles (impactor stage 1: > 4 μm; stage 2: 2-4 μm; stage 3: 1-2 μm; stage 4: 0.5-1 μm; stage 5: 0.25-0.5 μm; stage 6: <0.25 μm) (Winchester et al., 1979).

In summary, the chemical composition of the light scattering aerosols provides a valuable, if not the most important, clue we currently have regarding their probable sources. Sulfur compounds are evidently contributing about half of the fine particle mass over most of the continental U.S. They occur generally in the most effective light scattering size range, 0.4-0.7 μm, and there contribute 50% or more of the light scattering.

5. RELATIONSHIP BETWEEN AEROSOL PHYSICAL AND OPTICAL PROPERTIES

Ever since John Aitken developed a condensation nuclei counter, a quest has been in progress to establish a generally applicable quantitative relationship between aerosol concentrations and size and their effects on atmospheric optics. Aitken (1888) himself noted that at remote locations near the British sea shore, an increase of the condensation nuclei count was accompanied by a decrease of the visual range. In fact, he found that the product of the visual range (V) and the condensation nuclei count (CNC) was constant. This first quantitative "law" was supported by Wigand (1919) in Germany and he also refined Aitken's law by making V x CNC depend on the air humidity. The applicability and limitations of the visual range and CNC relationship was reviewed by Burckhardt and Flohn (1939), in which they came to the reasonable conclusion that the above product is highly variable in space and time and is of limited general use.

Early in this century Kimball and Hand (1924) followed up this work in the U.S. by determining the aerosol number concentration by microscopic counting of particles deposited in the Owens impinger. The device is a cross between a CNC and an impactor in that the air is first humidified and then impacted. According to Junge (1952), the Owens counter yields the total number concentration greater than approximately 0.2 μm. For Washington,D.C., and several other U.S. sites, the product of visual range times the Owens count (OC) has remained remarkably constant even without consideration of the relative humidity effect. In Britain, Wright (1935) conducted a similar study and confirmed that Kimball's value of the VxOC was also applicable for the fine particle population over Britain in the 1930's. These powerful regularities of aerosol optical behaviour prompted Linke (1943) to bring these developments to the attention of German scientists. In the postwar period there was little attention given to these valuable earlier observations.

A relationship that has received much more attention is that between the slope of the spectral extinction coefficient (Angstrom exponent) and the slope of the aerosol size distribution (Junge exponent). According to Angstrom (1929), the extinction coefficient or aerosol optical depth versus wavelength may be empirically fitted by a power law expression, λ^{-n}, where n is the Angstrom exponent. The Junge aerosol size distribution law also assumes a power law dependence of the aerosol concentration versus particle size, $n(\log r)\lambda^{-m}$. Mathematically, these empirical laws were consistent in that the power law size distribution along with the Mie theory for light scattering in fact yields a power law wavelength dependence of extinction (Junge, 1952). This consistency gave strong reinforcement to both Angstrom's and Junge's laws. Deviations from either law were called "anomalies" and were supposed to happen only "once in a blue moon".

In the early 50's Foitzik proposed that the measured spectral extinction data would be better fitted with a comparatively narrow lognormal distribution, centered around the wavelength of incident radiation, rather than with a power law function. Around 1960 Goetz and coworkers (1934) developed an aerosol centrifuge with high size resolution in the 0.1-1.0 μm diameter range and found that the size distributions exhibit a variety of shapes (usually not power law) depending on the sampling location. Fenn and Gerber (1960), and Fenn (1964) obtained high resolution size distribution data ($0.1<D_p<1.0$ μm) with a Goetz spectrometer and found,at a variety of locations, multimodal size distributions. He supported the multimodality of the "optical subrange" (0.1-1.0 μm) by measured aerosol phase function data for which the "best fit" size distributions were also multimodal. Foitzik (1964) used Fenn's size distribution data to calculate the corresponding spectral extinction values and concluded that these were more typical for many locations than those satisfying Angstrom's law. Badayev and coworkers (1975) at the Institute of Atmospheric Optics, Moscow, have measured the spectral extinction coefficient with

a transmissometer ($0.25<D_p<2.2$ μm) and inverted the size distribution of the typical haze. Their result is again a bimodal volume distribution within the fine particle mode, in accordance with Fenn's direct measurements. In spite of the compelling evidence presented by Foitzik, Goetz and Fenn on the limitations and use of Angstrom's and Junge's laws, they prevailed as the "accepted" aerosol models well into the 1970's.

In 1969 Whitby and coworkers (Whitby et al.,1972, Husar et al.,1972) performed an extensive set of size distribution measurements in the Los Angeles smog and proposed the "bimodal" distribution of aerosol volume, consisting of the fine particle mode $0.1<D_p<2.0$ μm and the coarse particle mode $2.0<D_p<20.0$ μm. The bimodal volume distribution has rapidly gained acceptance because it was supported by size distribution data from other locations and by the strong bimodality of the aerosol chemical composition. By the late 1970s the "Whitby distribution" was used for many applications where an aerosol "model" was required. It is, for instance, being incorporated in atmospheric electro-optical transmission models, such as LOWTRAN.

Unfortunately, the bimodal distribution still did not explain the observations of Fenn (1964): that the aerosol distribution (if measured with sufficient resolution) is multimodal within the fine particle mode (or "accumulation" mode), $0.1<D_p<1.0$ μm. This fine structure in size spectrum may be inconsequential for some applications, but has significance to aerosol optics: for a given aerosol mass the aerosol backscattering is dominated by particles in the size range D_p (0.3-0.8)λ, while the extinction coefficient per mass is strongest for $D_p = \lambda$.

By the 1970's, it was recognized that there are distinct advantages to monitoring the aerosol mass concentration in at least two size-segregated classes, the fine particle mass (FPM) and the coarse particle mass (CPM). The separation size is normally set at the saddle point of the bimodal mass distribution (1-3 μm). From physical considerations, first stated explicitly by Wegener (1911), most of the light scattering by haze is contributed by particles in the 0.2-2.0 μm size range. More recently there has been statistical confirmation of the strong relationship between the fine particle mass and the light scattering coefficient measured by the integrating nephelometer. In various parts of the country, simultaneous monitoring of b_{scat} and FPM yielded correlation coefficients exceeding 0.9, and the ratio of 3-4 m^2/g, as given in Table 2.

Table 2. Correlation of Fine Particle Mass with Light Scattering Coefficient

Location	m^2/g	r^2	N	Reference
Riverside,CA		0.88	88	Lundgren, 1970
Los Angeles,CA	3.7	0.69	39	Samuels et al., 1973
Oakland,CA	3.2	0.62	20	Samuels et al., 1973
Sacramento,CA	4.4	0.96	6	Samuels et al., 1973
Los Angeles,CA	3.2	0.83	58	White and Roberts, 1981
Portland,OR	3.2	0.90	108	Waggoner and Weiss, 1980
Mesa Verde,CO	2.9		5	Waggoner and Weiss, 1980
Puget Isl.,WA	3.0	0.94	26	Waggoner and Weiss, 1980
Seattle,WA	3.1	0.90	58	Waggoner and Weiss, 1980
Seattle,WA	3.2	0.94	64	Waggoner and Weiss, 1980
Denver,CO	3.3	0.96	268	Groblicki et al., 1981
Houston,TX	3.3	0.88	88	Dzubay et al., 1982

r^2 = coefficient of determination, square of correlation coefficient
N = number of points

The remarkable feature of these recent data sets is the narrow range of b_{scat} vs FPM

ratio for various sampling locations, times, etc. This ratio has units of m^2 of light scattering cross-section per unit mass of aerosol. It is thus a scattering efficiency factor, and its absolute magnitude is directly comparable to calculations of light scattering using Mie theory. The spatial-temporal invariance of the scattering efficiency factor has two possible explanations: either the size distribution of fine particles that contribute to light scattering is invariant or the scattering per unit mass of FPM is independent of particle size. As will be discussed later, it is a combination of both.

The above brief review, along with numerous reports not discussed here, reveals a century-long search for laws that describe the regularities of aerosol optics, aerosol size distributions and their interdependence. However, at this time, generally applicable laws that consistently describe the size distribution and optical properties of atmospheric fine particles are not at hand. The increasing need for electro-optical information about the atmosphere along with the encouraging hints gathered over the past century dictates that the search be pursued.

6. RELATIONSHIPS AMONG THE OPTICAL PARAMETERS

Data on the optical properties of atmospheric aerosols are much more abundant than aerosol properties obtained by nonoptical methods. It is therefore beneficial to search for regularities in the relationship of various aerosol optical parameters and ask what changes in the size distribution can explain the observed regularities.

Spectral extinction

The spectral extinction data of Foitzik (1938) and Middleton (1935) (Figure 14) show that the blue/green extinction ratio and the red/green extinction ratio converge systematically to unity as the extinction coefficient increases from near Rayleigh scattering to fog. Thus the spectral extinction of aerosol (defined by Middleton as air and particles) becomes increasingly "white" with larger values of extinction. An interesting abrupt transition from spectral to white scattering at $b_{ext} = 0.5\ km^{-1}$ has been used by Eldridge (1969) to define "mist", i.e. the transition phase between haze and fog. Middleton (1952) also brings to our attention the compilation of spectral extinction data by Wolff (1938) (Figure 15), who points out that the Angstrom exponent is essentially zero for visual range below 1 km but increases to about unity at 6 km visual range. For an aerosol-free Rayleigh atmosphere (about 200 km visual range), the Angstrom exponent should approach n=4.

Aerosol phase function

The regularities of the aerosol phase function (variation in scattering intensity with scattering angle) have also been examined, at least since the studies of Foitzik and Zschaeck (1953). They observed a systematic shift of light scattering toward forward angles with increasing extinction coefficient (decreasing visual range) (Figure 16). An impressive systematic follow-up investigation was conducted by Barteneva (1960) at 5 locations in the Soviet Union, also showing the elongation of the phase function with decreasing visual range. These regularities of phase function were also confirmed in the OPAQUE measurement program conducted in the U.S. and Europe using a polar nephelometer (Johnson et al.,1981) (Figure 17).

Backscattering

One of the more convenient means of monitoring the light scattering by aerosols is by detection of the light scattered backwards to the light source, whether the source be coherent or

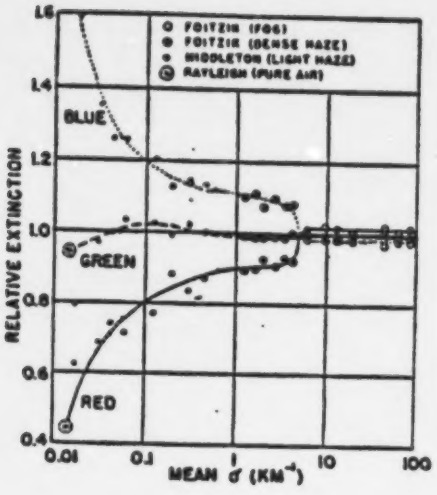

Figure 14. Mean values of relative extinction coefficient as a function of the three colors (Foitzik, 1938).

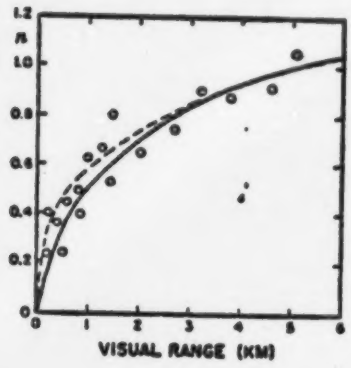

Figure 15. Relation between V and n (Wolff, 1938 summary with additional observations by Lohle, 1941).

incoherent. Curcio and Knestrick (1958) monitored the backscattering intensity (R) simultaneously with the visual range and obtained a remarkably well-defined relationship for Arcotta and Washington,D.C.: V=constant/$R^{1.5}$. In the USSR, Gavrilov (1966) reported an equally consistent relationship between total extinction and backscattering. Impressed by Barteneva's phase function data and the backscattering data of Curcio and Knestrick(1958), Fenn (1966) examined the consistency of these two data sets with favorable results: both the phase function and backscattering data show that with increasing extinction coefficient the backscattering phase function declines systematically.

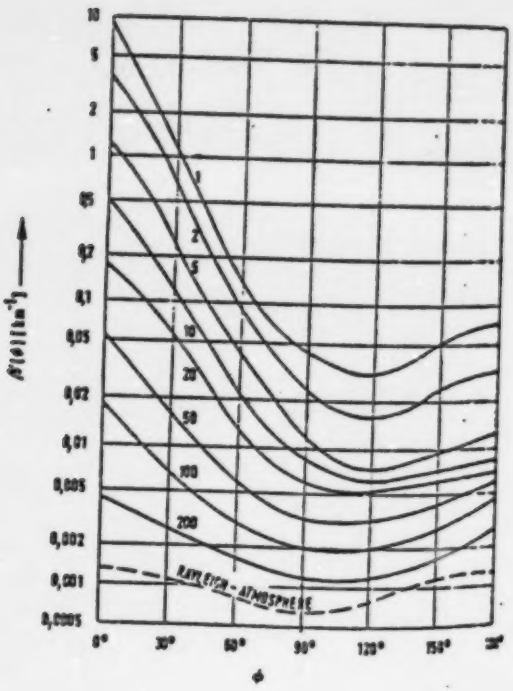

Figure 16. Variation of volume scattering function with scattering angle for several visibilities, measurements by Foitzik and Zschaeck, taken from Dietz (1957).

Barteneva (1960) reported measurements of aerosol phase function, calculated the light scattering asymmetry factor (ratio of forward to backward scattering), and plotted those against visual range. We first digitized her data and subsequently transformed it to a new coordinate system: asymmetry factor versus extinction coefficient (3.9/V) as given in Figure 18. The entire procedure including the digitization, transforming the axis, drawing and labeling the graphs was performed using interactive data manipulation and graphing software.

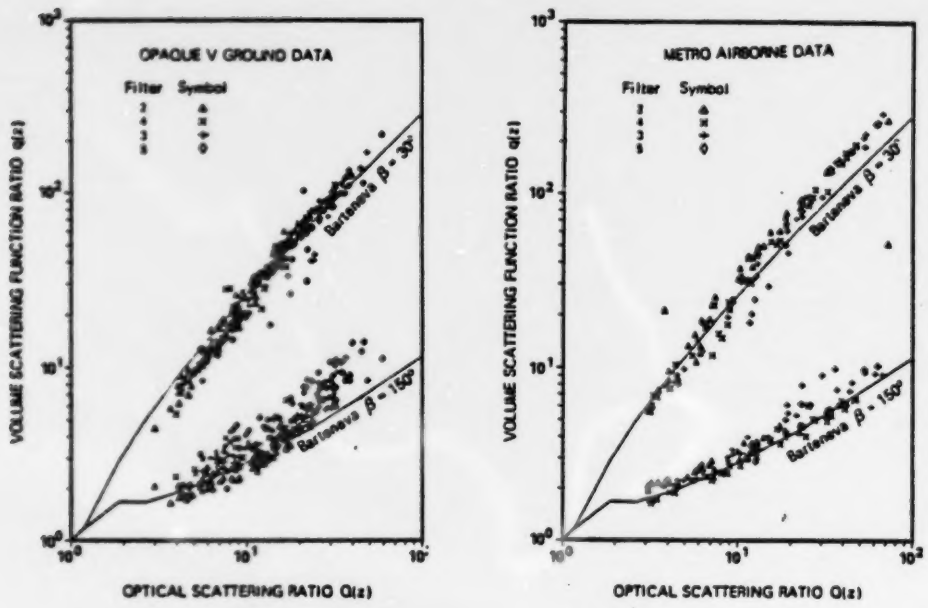

Figure 17. Comparison of multi-spectral directional scattering ratios measured by Visibility Laboratory airborne nephelometer (a) and ground-based nephelometer (b) with the photopic ratios from Barteneva (1960).

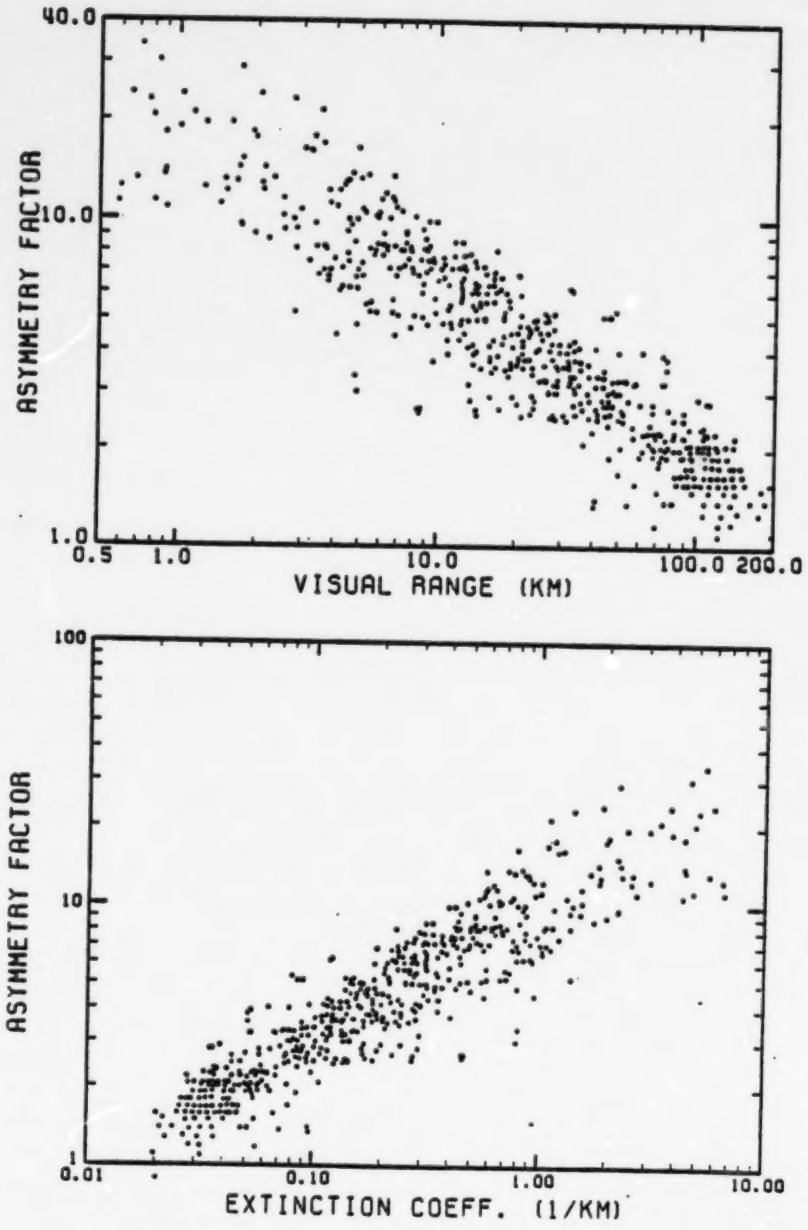

Figure 18. Asymmetry factor versus visual range (a) and extinction coefficient (b) using data from Barteneva (1960).

The merging and superposition of data sets from different investigators is illustrated in Figure 19. The backscattering intensities versus visual range data of Curcio and Knestrick (1958) were first digitized, plotted versus b_{ext}, and superimposed on similarly processed compatible data of Gavrilov (1966). The comparison shows the internal consistency of each set but a discrepancy (due to differences of the monitoring angle?) between the data sets. Once the literature data are computerized, they may also be subjected to statistical analysis, e.g. correlations.

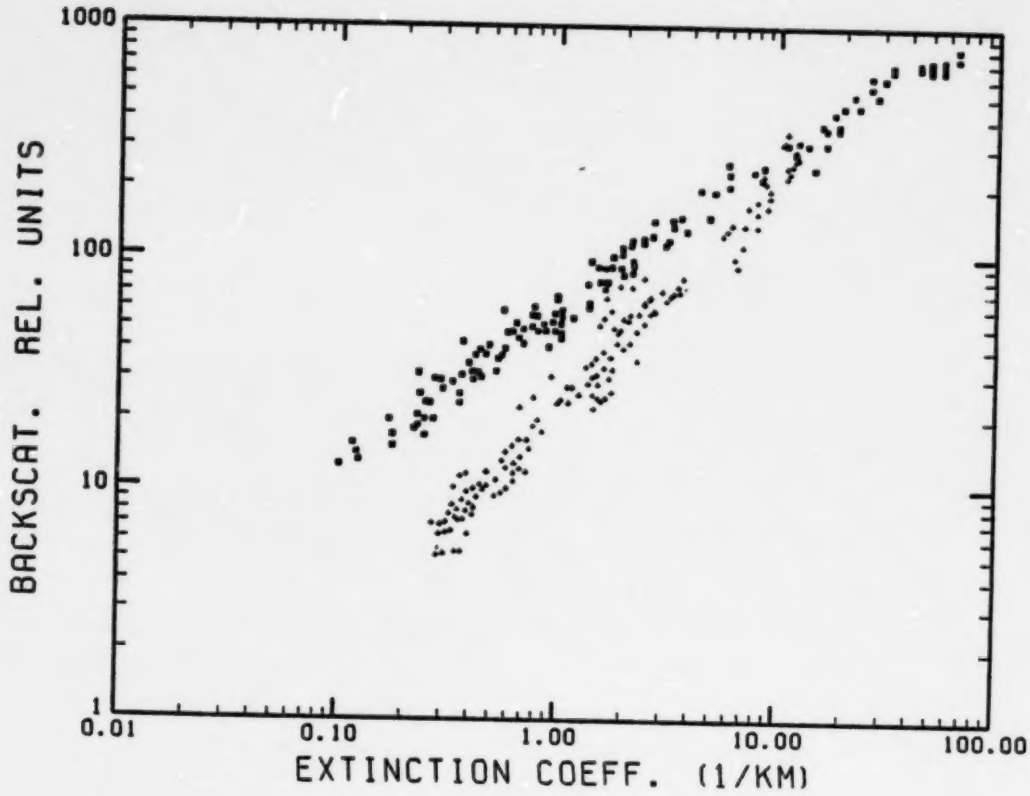

Figure 19. Backscattering intensities versus visual range, data from Curcio and Knestrick (1958) and Gavrilov (1966).

7. INVERSION OF OPTICAL DATA USING INTERACTIVE GRAPHICS

Measurements of spectral extinction and the aerosol phase function are inverted to aerosol size distributions using CAPITA's interactive graphics capabilities. The approach is illustrated in Figure 20, using spectral extinction data. Conceptually, the scheme is identical to that described by Volz (1954). The aerosol size distribution, displayed as a volume distribution function ($dv/dlogD_p$), is expressed as a sum of a set (11) of narrow distributions, covering the size range 0.1-10 μm. The contribution of each size range to the light extinction (per unit aerosol volume) is precalculated for several values of imaginary and real refractive index. At fitting time,

the investigator uses the refractive index of his choice. The thus calculated contributions to light extinction by each size class are shown as thin lines in Figure 20. The fine tuning of the fitting is facilitated by a crosshair on the terminal that allows raising or lowering the concentration in each of the 11 size ranges until a satisfactory match of data points and the calculation is obtained. It should be understood that these size distribution do not exist in reality but are merely a modeling tool.

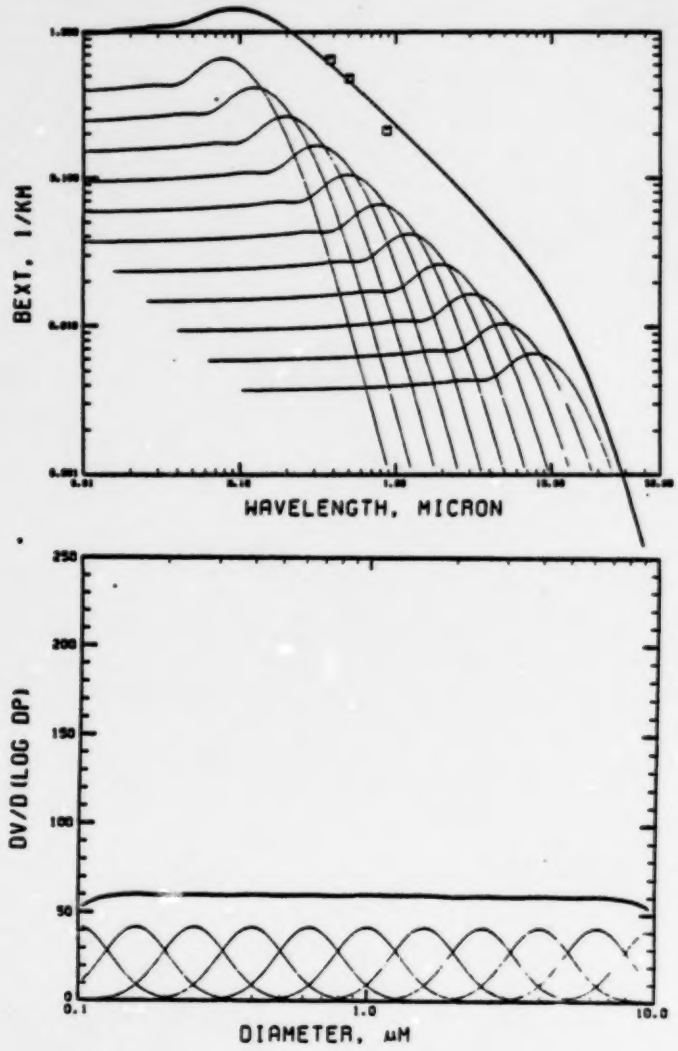

Figure 20. Aerosol size distributions from spectral extinction data.

For illustration purposes, we use here the inversion of spectral extinction data reported by Curcio et al. (1961). The heavy solid lines indicate the best fit extinction coefficients obtained for Curcio's data sets numbered 1, 2 and 3 (Figure 21). Fit of spectrum 1, for instance, shows

that in order to fit the data points at 0.4 and 0.5 μm wavelength, it was necessary to add a rather large amount of aerosol volume at around 0.2-0.3 μm. Also, the change in the slope of the Angstrom exponent for 2 μm wavelength necessitated the addition of a large aerosol volume at about 5 μm.

Another interesting data set was reported by Badayev et al. (1975) from the Institute of Atmospheric Optics, Moscow. As pointed out by the authors themselves, the spectral extinction data for type A haze can only be fitted by a multimodal volume distribution with modes at 0.15, 0.7 and 4 μm (Figure 22). Badayev et al. noted that such spectral extinction data which do not satisfy Angstrom's power law occur frequently.

The interactive graphics fitting approach also gives an immediate illustration for the uncertainties of the inversion. An alternative set of volume distributions can provide an identical quality of fit. It is apparent that the extreme volume modes, at 0.15 and 4 μm (Figure 22), constitute a "minimum" volume necessary for the fit. The actual volume distribution below 0.3 and above 3 μm is probably more but cannot be determined because of the non-uniqueness of the inversion. This feature also demonstrates that spectral extinction data can yield information only about the size distribution range that corresponds roughly to the wavelength range of the spectral measurements.

If, for instance, the spectral extinction data are obtained for the 0.4-0.1 μm wavelength range, it is hopeless to seek inverted size distribution values below 0.4 and above 1 μm (a fact frequently overlooked by investigators). It is for this reason that Badayev et al. strongly recommended measurement of spectral extinction from about 0.25-0.3 μm upward. The spectral extinction data for haze types B and C can be fitted with much broader and less bumpy aerosol volume distribution functions.

Aerosol size distributions can similarly be fitted iteratively to measured phase function data. An attractive data set for illustration and other purposes is the set measured and tabulated by Barteneva (1960). Figure 23 shows the measured phase functions (crosses), the calculated phase functions for three values of the real part of the refractive index (solid line), the best-fit volume distribution function, and finally the spectral extinction coefficient calculated from the volume distribution function. Again it should be understood that these fits are not unique and that the atmospheric aerosol is not necessarily made up of two volume distributions. More likely the real distribution is a weighted average of the two. The use of two volume distributions, however, is a useful modeling tool.

This numerical fitting process illustrates that for light hazes the choice of the real refractive index is not crucial. For heavy haze (# 8), on the other hand, a fit can only be obtained with n = 1.4 or 1.33 but not with 1.5 or 1.6. The best fit size distributions also show that for light haze (# 4 and # 5) an appreciable quantity of 0.15 μm size particles is required in addition to Rayleigh scattering in order to obtain the measured amount of backscattering. Heavy hazes (# 7 and # 8) can be fitted with a narrower size distribution with volume mean diameter centered at the wavelength of light. It is also instructive to note that the calculated spectral extinction data corresponding to Barteneva's light hazes (# 4 and # 5) roughly satisfy Angstrom's law with exponent declining from 1.5, for heavy hazes, to 0, for haze. The haze (# 8) actually exhibits "anomalous extinction" between 0.3 and 0.6 μm wavelength.

8. COMPARISON OF MEASURED AND INVERTED SIZE DISTRIBUTIONS

There are two "regularities" emerging from the extensive aerosol-optical data sets on fine particles: the systematic forward elongation of the aerosol phase function with increasing ex-

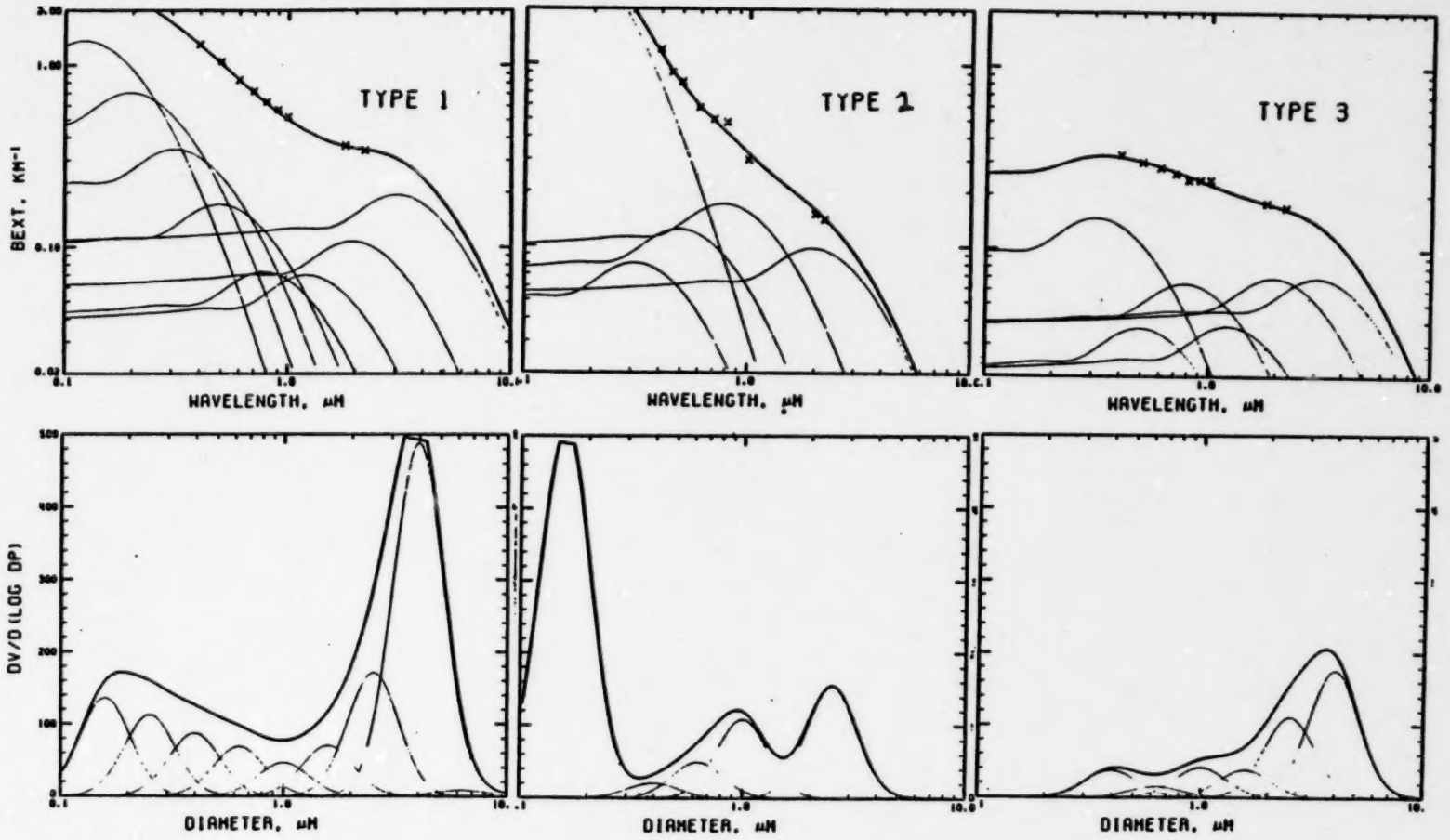

Figure 21. Spectral extinction and corresponding size distributions, data from Curcio et al. (1961).

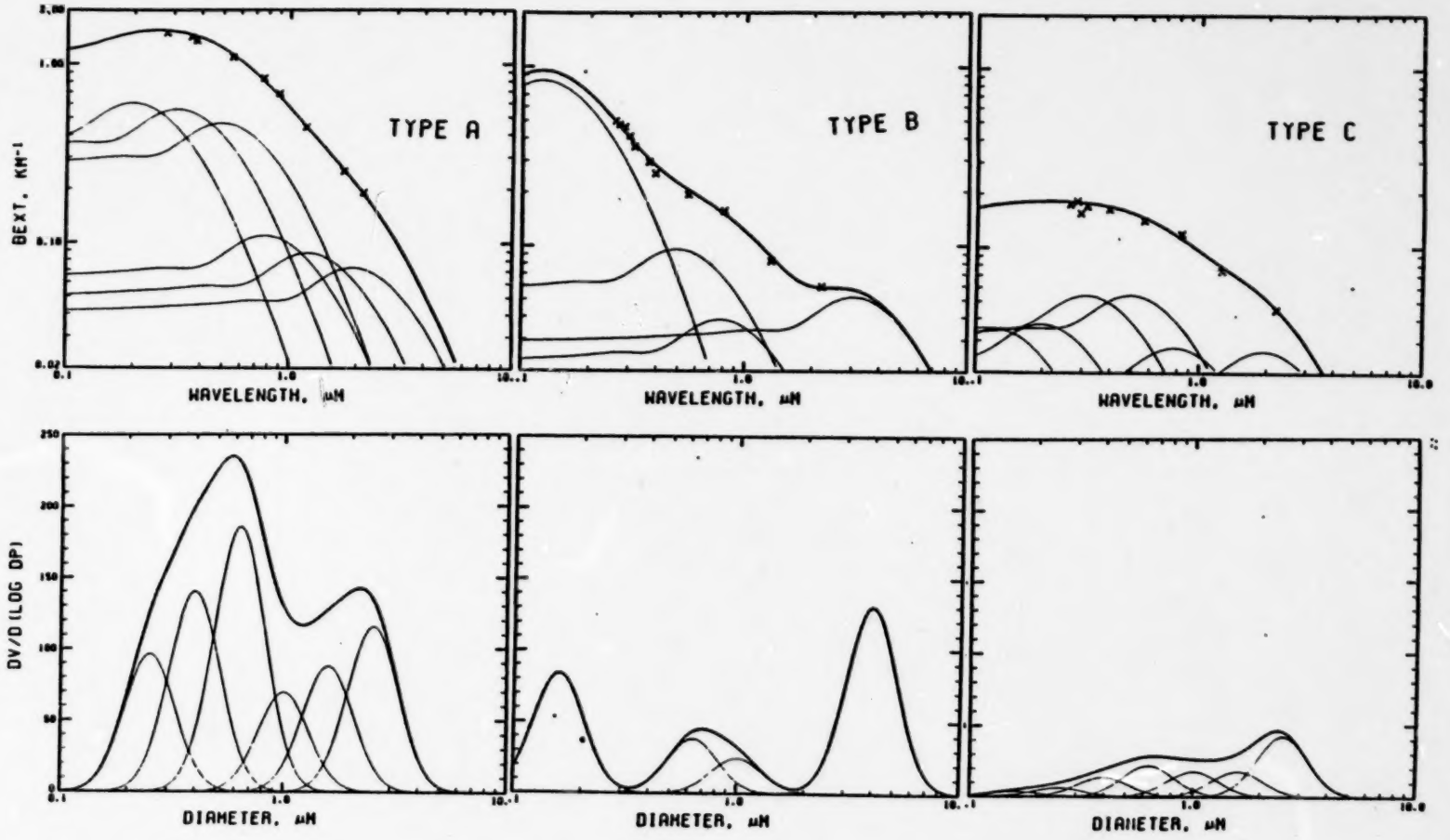

Figure 22. Spectral extinction and corresponding size distribution, data from Badayev et al. (1975).

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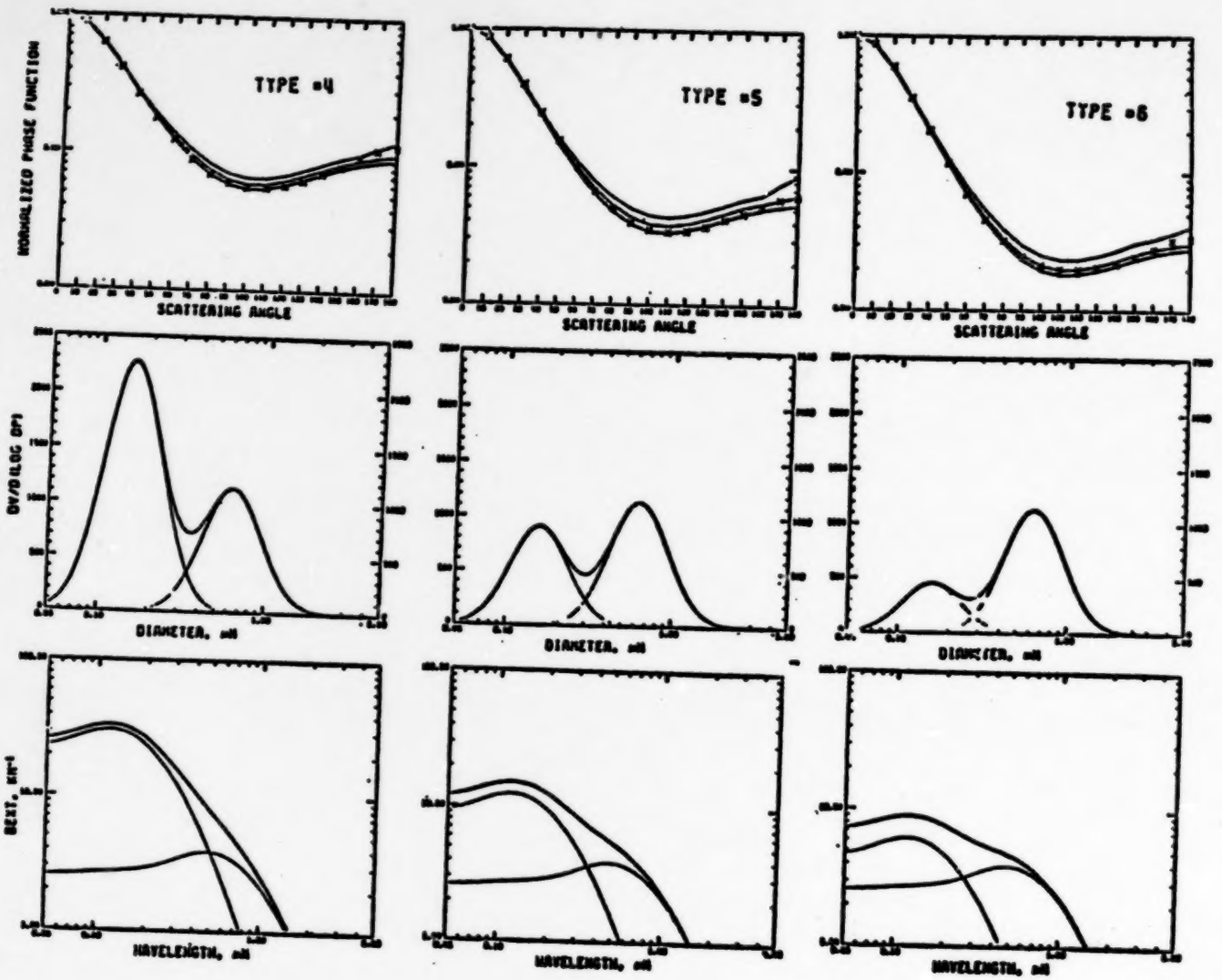

Figure 23a. Phase function data with corresponding size distributions and resulting spectral extinction, data from Barteneva (1960).

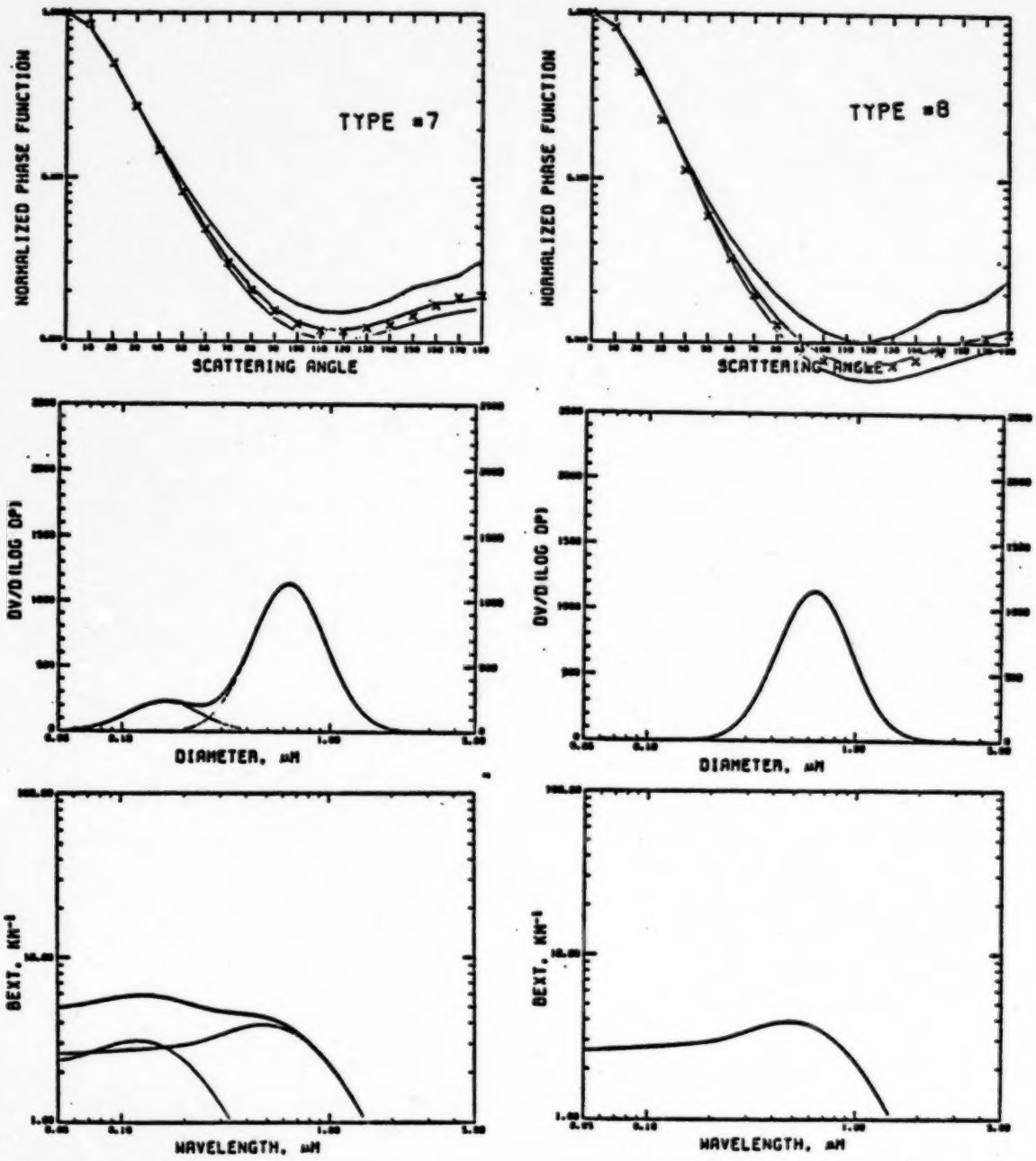

Figure 23b. Phase function data with corresponding size distributions and resulting spectral extinction, data from Barteneva (1960).

tinction coefficient (Foitzik, 1965, Barteneva, 1960, Johnson, 1981) and the existence of the "accumulation" mode, i.e. condensational coagulation aerosol growth into a relatively narrow size range (Husar et al., 1972). For some time it has been felt that the fine particle mass mode is rather invariant in volume mean diameter. This however is inconsistent with the inverted size distributions from Barteneva's phase function data (Figure23). There, it was necessary to increase the volume mean diameter from 0.3 to 0.6 μm corresponding to light and heavy haze respectively.

One possible explanation for this may be experimental error in either the phase function or the size distribution data sets. It is known, for instance, that size distributions measured by the electrical mobility analyzer tend to be broadened by cross channel interference. Interesting new data sets on the mass-size distribution of particulate sulfur (Reible et al., 1982) show substantial structure in the distribution from one location (aerosol age) to another (Figure 24). It is therefore conceivable that the broad "grand average" fine particle distribution (the "Whitby distribution", Figure 25) with $D_p = 0.3$ μm and $\sigma_g = 2$ may be better represented by a combination of several lognormal distributions within the fine particle modes which will be relatable to easily measurable atmospheric parameters such as visual range or aerosol mass concentration.

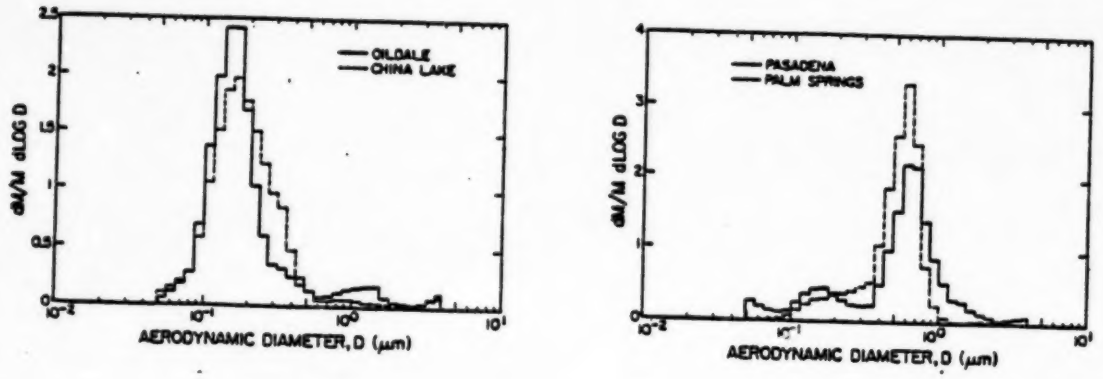

Figure 24. Normalized ambient aerosol sulfur mass distributions(Reible et al. 1982).

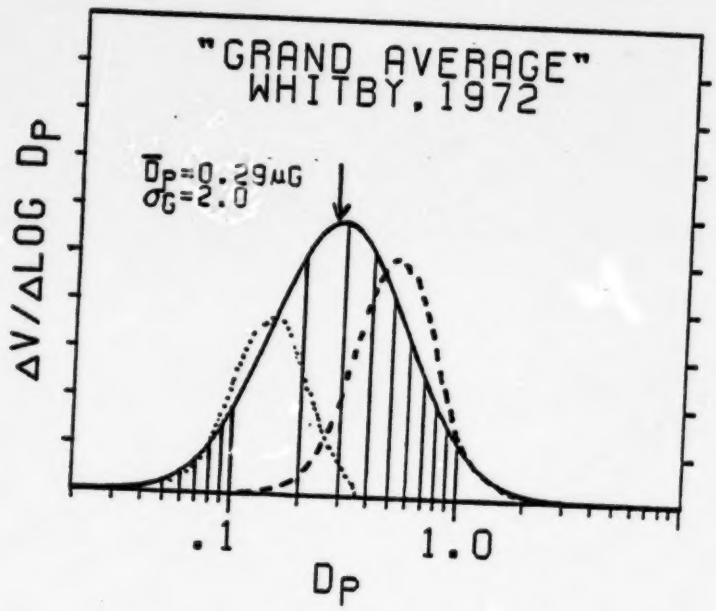

Figure 25. "Grand Average" fine particle distribution ("Whitby distribution") (Whitby et al. 1972).

9. PHYSICAL EXPLANATIONS FOR THE OBSERVED REGULARITIES

As soon as atmospheric data were generated showing well behaving relationships among the aerosol-optical parameters, attempts were made to explain them based on fundamental physical laws. By far the most important tool for that purpose is the "Mie theory" which describes quantitatively the interaction of spherical particles with electromagnetic radiation. Thus the calculation of essentially all of the optical properties (the Stokes matrix) can be performed in a straightforward manner for any polydispersion provided the size distributions and refractive indices are known. The main difficulty in performing consistency tests among the aerosol-optical parameters arises from the fact that the size distributions and refractive indices of the aerosol population were not known. Also the role of specific processes that shape the aerosol size distribution was highly uncertain.

Following the Krakatoa eruption in 1883, the abundance of optical data prompted investigators to seek information about the aerosol size distribution via "inversion" or deconvolution of the optical data. As early as 1884, Kiessling concluded that the spectacular optical phenomena worldwide were caused by the volcanic dust with characteristic size between 1 and 2 μm. Wegener (1911) used simple but most elegant reasoning (without involving the Mie theory) when he stated that most of the atmospheric haze that scatters the visible light is comparable in size to the wavelength of light. Goetz (1934) brought to the attention of atmospheric scientists the solution of the Mie equations by Stratton and Houghton (1931) who calculated the scattering efficiency factors for increasing particle diameter-wavelength ratios. Given the haze optical properties and Mie theory, size distributions were sought that "explained" the data. Penndorf (1954) "inverted" the spectral extinction data obtained in Europe following a major forest fire in western Canada. He concluded that the peculiar blue sun and blue moon phenomena of that time were due to aged forest fire smoke of 0.6-0.8 μm. Volz (1954) gave a most illuminating graphical illustration of the influence of individual particle size classes on the extinction coefficient in different wavelengths. (We have adopted the Volz technique of "inversion" for use with modern interactive graphic software and hardware described in the next section). In the 1940's Siedentopf (1947) measured the aerosol phase functions and concluded that they could be explained by a relatively narrow watery haze size distribution in the diameter range 0.3-0.8 μm, supplemented by a few opaque coarse dust particles.

With the advent of computers numerous inversion (automatic fitting) procedures were developed to extract aerosol size distributions from spectral or angular scattering data. While we accept the utility of such automated fitting procedures we prefer interactive, iterative fitting controlled by the investigator. Such an approach gives the user a much better feel for the non-uniqueness and uncertainty range of the fitting process.

Humidity effects

Well before the turn of the century it was known that hygroscopic light scattering particles will grow in size and scatter more light with increasing humidity. By the early part of this century Hagman (1865) recognized that the equilibrium size of hygroscopic particles is determined by the balancing of two forces: surface tension that increases the pressure within the particle and pressure depression due to dissolved salts. The theory of particle growth was first formulated by Gudris and Kulikowa (1924). Kohler (1936) developed and applied salt solution theory for the growth of sea salt particles with RH. He also calculated the critical supersaturation necessary for the nucleation to occur as a function of particle size. Since Kohler the aerosol growth with humidity is probably one of the most belabored subjects in the atmospheric sciences literature. It will not be further discussed here except to note that accounting for relative humidity effects will be an essential part of any parameterizations.

Coagulation

Based on direct microscopic observations of the morphology and composition of urban particles, Whitelaw-Gray and Patterson (1932) proposed that coagulation should be an important mechanism shaping the size distribution of atmospheric aerosols. Later, Junge (1952) also concluded that the lower end of the aerosol size distribution, below 1.0 μm, is determined by the balance between the sources and coagulation decay of particles. Numerous studies since then confirm that coagulation among the haze particles particularly below 0.5 μm is an important process shaping the size distribution.

Sedimentation

The removal of large particles by sedimentation is a plausible mechanism that determines the shape of the size spectra for the range above a few microns. The atmospheric lifetime of coarse particles is also determined by sedimentation. The first physical explanation of Junge's power law size distribution laws was provided by Friedlander (1960). He proposed that the atmospheric aerosols exhibit similar (power law) shapes because the input rate of fine particles from various sources is balanced by the coarse particle removal rate by sedimentation. He also proposed that coagulation provides the mechanism for the transfer of particles from fine to coarse sizes. Taking the analogy from the cascading transfer of turbulent energy from large to small atmospheric eddys, Friedlander termed the equilibrium size distribution, balanced by coagulation and sedimentation, as the "self preserving distribution."

It is now realized that self-preserving size distribution of the accumulation mode is due to the piling up or accumulation of material in the size range between 0.1 and 1.0 μm. There is very little transfer of material from the fine to the coarse mode.

Gas Particle Conversion

Observing the rays of sun soon after rain, Rafinesque (1817) was forced to the conclusion, as many "philosophers" before him, that in the "chemical laboratory of the atmosphere" there must be "in situ" processes responsible for the haze visualizing the rays of sunlight. Tyndall (1869), Aitken (1888) and many others confirmed that chemical aerosol formation occurs in the atmosphere at significant rates. Haagen-Smit (1952) in his key contribution to the chemistry and physiology of the Los Angeles smog documented that man's activities contribute significantly to this chemically formed haze. The roles and interaction of nucleation, coagulation and condensation in the dynamics of the smog aerosol were established and numerically formulated by Husar et al. (1972).

Cloud scavenging and removal

Cloud processes influence the aerosol dynamics in two ways. In a volume of atmospheric air, once cloud or fog condensation occurs, the much finer haze particles are scavenged efficiently by the less populous cloud droplets. This results in a collection and mixing of several haze particles into one cloud droplet. Following the evaporation of the cloud droplets, the new, internally mixed, fine particles will be much larger in size than before the scavenging. This physical collection and growth is frequently augmented by chemical conversion of gases within the cloud droplets. Secondly, cloud scavenging and subsequent rainout constitutes the most important removal mechanism for atmospheric haze particles. While both of these processes are of vital importance for the dynamics of the fine particle size spectrum, they have eluded quantification in the past.

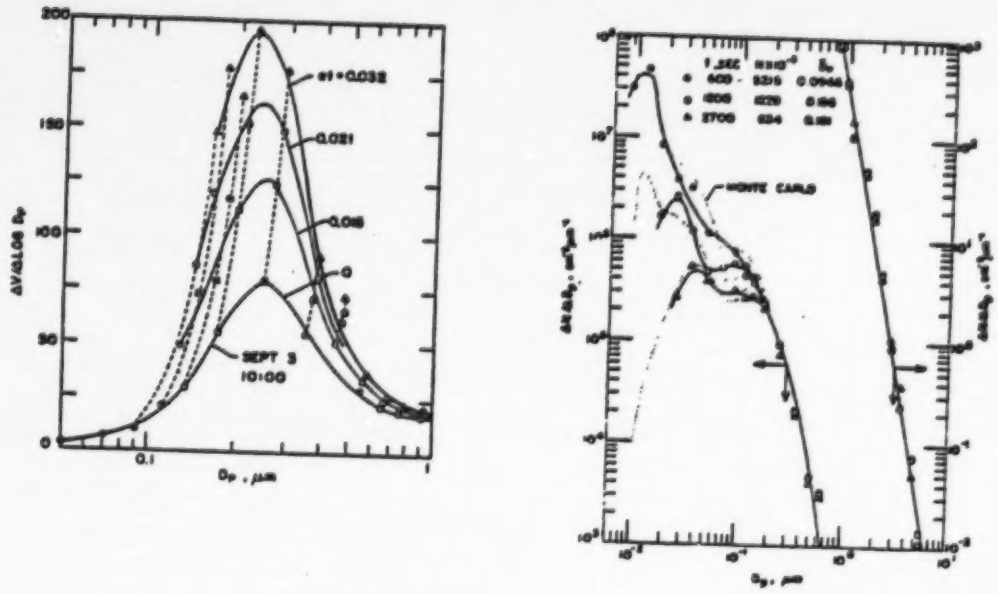

Figure 26. Volume and number distribution computed by Monte Carlo size distribution simulation code.

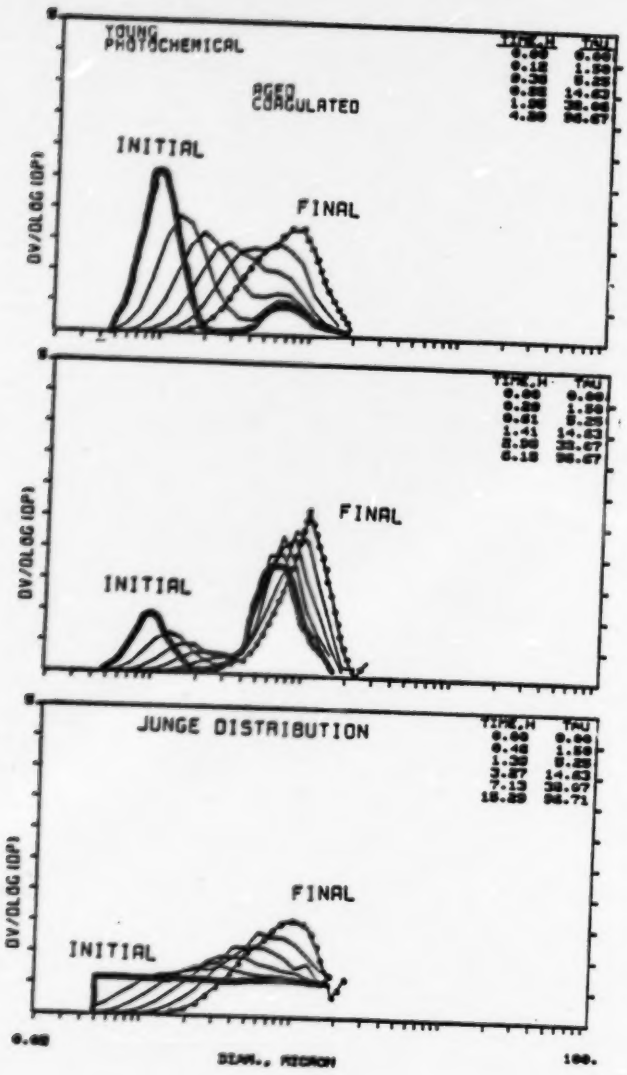

Figure 27. Simulations of atmospheric coagulation and condensation.

It is apparent that our current understanding of the processes that determine the fine particle size distribution at any given time and location is inadequate. The fundamental physical laws that dominate the size spectrum such as source strength, atmospheric mixing, nucleation, condensation, coagulation and cloud processes are, in principle, understood. The problem lies in knowing the proper sequence and rate at which these processes act under ambient conditions. Furthermore, the long atmospheric lifetime of fine particles ranging from a day to weeks requires the knowledge of the previous history of the aerosol population over days or weeks. While this may appear to be a formidable task it is our judgement that the quest for development of atmospheric aerosol models based on physical rather than empirical laws is a meaningful and rewarding undertaking.

10. PLAUSIBLE EXPLANATIONS FOR THE OBSERVED SIZE DYNAMICS

Field measurements and the empirical laws that summarize them provide us with the facts, i.e. the pattern of aerosol behavior, but they do not explain their cause. Diagnostic models of the aerosol size spectrum dynamics can provide plausible explanations (but generally no proof) for the observed phenomena. The approach is illustrated in Figure 26 showing simulations of atmospheric aerosol coagulation and condensation. During the 1969 Pasadena smog study it was observed that the aerosol size distribution below 0.2 μm decayed systematically every night. In order to test whether coagulation could explain the observed decay, a laboratory and a numerical Monte Carlo simulation of the observed process was conducted. In was concluded that coagulation could indeed decay the lower part of the size spectrum night after night. Similarly, the daytime aerosol growth of the size distribution was simulated by diffusional deposition of condensable gaseous products (Fig 26). The diagnostic growth simulation revealed that diffusion controlled deposition is indeed a likely and plausible explanation for the growth of 0.1-1.0 um aerosol. It also showed, however, that it was necessary to impose a cutoff at 0.09 μm particle size, below which growth did not occur. Tentatively, the physical explanation given was the "Kelvin" cutoff, i.e. that surface tension does not allow growth of particles below a given size.

Numerical experiments have been conducted with the Monte Carlo size distribution simulation code, with objectives similar to the ones set out by Junge and Abel (1965): given an initial volume distribution function, what are the aerosol growth kinetics due to coagulation for 3-5 days? This simulation suggests that, given an aging time of 5 days at 10 $\mu g/m^3$ (or 0.5 day at 100 $\mu g/m^3$), the resulting volume distribution function will be similar regardless of the initial volume distribution function; thus, the aerosol will approach a self-similar shape (Figure 27). It is important to recognize, however, that wet and dry removal and cloud scavenging - evaporation processes also play a very significant role in the aerosol size spectrum dynamics. The role of these processes remains to be explored.

By far the most challenging and most rewarding task will be to give physical explanations for the regularities documented by Barteneva (1960) and Johnson (1981). The puzzling feature of their observations is the lack of the explicit dependence of the phase function on relative humidity. Evidently, it is not important whether the increase of extinction coefficient is due to water uptaLe by hygroscopic salts, coagulation, gas-particle conversion of condensable species or aggregation by cloud droplets. The resulting growth in aerosol (and forward shift in light scattering) is roughly the same regardless of the mechanism as pointed out by Johnson (1981). This has exciting implications to the modeling of fine particle optics.

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